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THE UNIVERSITY OF ALBERTA

EVALUATION OF A NEW PROCESS FOR THE MANUFACTURE OF

CARBON BLACK FROM LIQUID HYDROCARBON

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE  
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by

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## I. ABSTRACT

A semi-pilot plant evaluation of a new process for making carbon black from liquid hydrocarbon feed-stocks has been made. The process is autothermic in that no external heating source is required. Different hydrocarbons may be used for the feed and the fuel. The process is characterized by the fact that stoichiometric quantities of fuel (in this case, natural gas) and air (or oxygen) are burned in special tunnel-type "surface combustion" burners. Combustion is essentially complete before the combustion product gases enter the reactor proper. The sensible heat of these gases is then used to bring the liquid feed up to reaction temperature and to supply the heat of reaction. Conventional carbon black collection methods were used.

Two feed stocks were investigated - diesel oil, for the bulk of the runs, and benzene. The carbon black produced was sent to a major rubber company where it was compounded with rubber. The resultant rubber was then subjected to standard tests. The results showed that the carbon black may be classified as a semi-reinforcing-furnace (SFR) black. This is a general purpose black, extensively used for compounding rubbers to improve the latter's tensile strength and abrasion resistance.

Only a limited range of reaction times was investigated. Consequently, the yield was primarily a function of the temperature of the reaction zone. Optimum yields were realized at a furnace temperature of around 2200°F at which temperature, the yield on a carbon basis, was around 44% for a diesel oil feed and 57% for a benzene feed.



In such a small scale furnace, large heat losses were unavoidable and thermal efficiencies ranged from 56% to 85%. In larger installations, heat losses would be negligible and this would be reflected in substantially higher carbon black yields. Since yields and quality are apparently as good as and perhaps superior to those for existing processes, the present process appears rather promising but more work is indicated.





## II. INTRODUCTION

Carbon black is the generic name of an important class of very fine and fluffy industrial carbon produced from natural gas, oil enriched gas or petroleum oil. Scientifically, it may be defined as minute solid particles consisting of "predominately" (80-95% or more) quasi-graphitic carbon of average particle size in the colloidal range of 1-500 milli- $\mu$  (1). From an industrial point of view, it is differentiated from lamp black by having a particular rubber-reinforcing property which increases the resistance power of the compounded rubber against abrasion. On the other hand, lamp black, which is a comparatively coarse and gritty black produced from incomplete combustion of carbon-containing materials, does not possess any significant rubber-reinforcing property. Although the true mechanism of the rubber-reinforcing property of carbon black has not been clearly established and accepted, yet this property can be strikingly demonstrated in terms of the road-wear of a tire. If an equal volume loading of an inert filler was used in tire tread, the maximum road-wear expected would be around 3,000 miles. Whereas the road-wear of a modern tire reinforced with carbon black is some 30,000 to 45,000 miles. (2, 3).

The average 6:00 x 16 passenger tire contains about 4 pounds of carbon black. The major use of carbon black is in rubber industry, (4) and only a total of several percent is used in pigment and printing ink.

Industrial carbon blacks, which are in greatest production, are, in the order of their appearance in the carbon black industry of North America, channel black, thermal black, furnace black and oil black. The



first U.S. patent on carbon black manufacture was granted to Adolph Millochau of New York city. In North America, the first impingement plant was erected in New Cumberland, (5) and the first patent for channel black production was granted to L.J. McNutt in 1892. Until just before the Second World War, channel black dominated the field of carbon black manufacturing, and just prior to the Second World War, a patent was granted for making oil furnace black.

More than 690,000 short tons of carbon black (which is about ten times the production rate of 1940) were produced in U.S.A. in 1950, and 840,000 short tons in 1951. The U.S. carbon black industry accounted for 97% of world production. The carbon black consumption in Canada is shown in Table 1.

CARBON BLACK CONSUMPTION IN CANADA (6)

Year	Inks	Paints Pigments etc.	Oil Cloth etc.	Polishes etc.	Pulp Paper	Rubber Products	Total lbs.
1953	1,439,389	351,483	31,953	19,421	98,000	54,363,312	56,303,558
1954	1,684,000	476,000	17,000	18,000	106,000	48,489,000	50,790,000
1955	1,679,000	313,000	29,000	18,000	118,000	55,724,000	57,881,000
1956	1,781,000	546,000	26,000	17,000	121,000	68,536,000	71,027,000
1957	1,906,000	484,000	23,000	18,000	119,000	65,352,000	67,902,000

Table 2 shows the Canadian imports of carbon black.

CANADIAN IMPORTS OF CARBON BLACK (lb.) (6)

Year	1950	1951	1952	1953	1954
Quantity (lbs.)	56,364,107	57,686,603	58,113,639	57,376,174	39,055,182
Year	1955	1956	1957	1958	
Quantity (lbs.)	46,692,942	42,401,103	40,184,591	31,285,976	





Table 3 shows Canadian exports of carbon black.

CANADIAN EXPORTS OF CARBON BLACK (lb.) (6)

Year	1950	1951	1952	1953
Carbon Black (acetylene, carbon, gas, lamp. lbs.)	13,621,667	15,683,206	12,518,313	15,279,625

Year	1954	1955	1956	1957
Carbon Black (acetylene, carbon, gas, lamp. lbs.)	15,388,714	--	--	--

Year	1958
Carbon Black (acetylene, carbon, gas, lamp. lbs.)	--

Table 4 shows carbon black consumption by Canadian rubber industry.

CARBON BLACK CONSUMPTION BY CANADIAN RUBBER INDUSTRY (6)

1956		1957	
Quantity (lbs)	Cost at works (dollars)	Quantity (lbs)	Cost at works (dollars)
68,535,700	5,908,000	65,351,733	5,620,479

The use pattern of carbon black in Canada in 1956 was as follows: (7)

Channel black	15,000,000 lbs.	22%
gas furnace black	23,000,000 lbs.	34%
oil furnace black	30,000,000 lbs.	44%
Total	68,000,000 lbs.	

From the manufacturing point of view, the development of carbon black can be divided into three eras:-





1. The lampblack era. This era was of but little significance, since all the lamp black was used only as pigment for paints and inks.

2. The natural gas era. During this era, the major production of carbon black was almost exclusively from natural gas. Three major kinds of carbon black were produced in this era, i.e., channel black, furnace thermal black and furnace combustion black. Channel black is by far the best for natural rubber, but the price is higher than that of the other two. Furnace thermal black and furnace combustion black possess lower rubber reinforcing power and less blackness in inks than channel black, but they are somewhat cheaper because of their higher yields. Furnace blacks from natural gas furthermore can be used in larger quantities in compounding synthetic rubber with low heat generation, while still maintaining the elasticity and rebound of the rubber. Therefore their demand rose with the great increase in the consumption of synthetic rubber. However the present trend is towards the use of oil blacks for compounding synthetic rubber, and the rush for furnace black from natural gas is over. (8) Moreover the removal of some of the liquid constituents from wet natural gas (by natural gasoline plants) not only decreases the yield of carbon black, but in some cases also lowers the quality. Although the present trend in the carbon black industry is towards the increasing production of oil black, there remains a demand for a certain quantity of channel black. Since the channel black plants are relatively simple, they can be moved from one isolated gas field to another isolated gas field which has not been connected by the pipe lines. Therefore, it will take some time before the channel blacks are completely displaced by oil blacks in rubber uses.





3. The oil furnace era. In this era, the majority of the carbon black is made wholly from liquid hydrocarbons or from natural gas with oil enrichment. The reason for the increased use of oil furnace blacks is that they are better suited to both synthetic and natural rubbers than any blacks previously available. Besides this technical preference, the rising price of natural gas gives the oil black process an increasing economic advantage.

There are two aspects of the carbon black industries at the present time which should be pointed out. First, from the technical point of view, there has been a switch in raw material from gas to oil and the nature of combustion has been changed from unconfined combustion to combustion in a furnace. Secondly, from an economical point of view, the location of carbon black plants is market oriented, rather than raw material oriented because of the lower transportation cost of liquid raw materials as against that for gas or the finished product.

Although some more expensive mineral reinforcing pigments are used for colored or white rubber, and in England and U.S.A. lignin is used to a small extent for reinforcement of rubber, yet carbon black continues as the best reinforcing agent for rubber compounding. However, the chief future threat to carbon black may be presented by silica. (9) It is now possible to obtain silica at a price which is at least competitive with carbon black. In polar elastomers, such as carboxylic rubbers, vinyl pyridine rubbers or silicone rubbers, the silica fillers show their best effect and give compounds with superior properties to those of corresponding black stocks. However in most products, such as tire tread, the properties of the silica reinforced



elastomer are not quite as good as those of a comparable black compound. Therefore in the foreseeable future, it is unlikely that carbon black will be extensively replaced by other reinforcing agents. At present, about 90-95% of carbon black sales in Canada goes to the rubber industry.

The present research and development of carbon black may be summarized as follows:

- A - continuous effort to increase yield and efficiency
- B - continuous effort on developing oil blacks of still finer particle size.
- C - search for new and better product: Philliph Petroleum Co. first announced the new SRF black which imparts 25-30% better tread wear to tires than previous blacks.
- D - considerable work is done with electron microscope and X-ray diffraction techniques in studying crystal structure of carbon black as related to its behavior.
- E - fundamental research about the nature of carbon black reinforcement of elastomers and the effect of chemical groups at the black surface (10). A number of investigators are working on the treatment of carbon black surfaces to provide just the right chemical atmosphere for good reinforcement, i.e. for high chemical interaction with the surrounding rubber (9). Recent work along these lines by Walker, Dannenberg and Boonstra at Cabot (11) who oxidized black by different treatments, showed the considerable effect this may have on the physical properties of the compounded elastomer.





F - new uses

i - incorporation in roads to reduce glare

ii - in making flexible heating tape (12). A tape of woven glass fibres, which is impregnated with silicone rubber, is made conductive with carbon black.

iii - the addition of carbon black to liquid fuel will increase the flame radiation because of extra emissivity (13). A production trial carried out by the Shell Development Co. (14) and the Bethlehem Pacific Coast Steel Corporation showed that a 5% carbon black addition to fuel oil resulted in a reduction of about 10% in the fuel consumption per ton of steel made and a reduction also of about 10% in the change to tap time in an open-hearth furnace (15, 16).

iv - in plastics. Recent developments showed that carbon black could have a very brilliant market in the plastics industry (17, 18). Small amounts have been used for coloring and to protect against degradation from sun and weather. However, larger quantities will cause brittleness and cracking, in the compounded plastics. Recently, however a new processing technique was developed, which claimed for the first time a large scale, 50 to 75% by weight, use of carbon black in plastics (19, 20, 21, 22, 23, 24 and 25). By large-scale admixture of carbon black in the new process the two most serious weak points - creeping and cracking - of plastics were said to be virtually overcome. Most important of all laboratory tests indicated that the burst strength of the pipe was doubled.



The General Economics of Carbon Black Industry

The world market for carbon black is closely and directly related to the consumption of rubber which accounts for about 94% of all carbon black produced.

In 1953 the carbon black production by the Western World was estimated to be 855,000 tons (26) in which furnace black was 544,000 tons, channel black 236,000 tons, thermal black 45,000 tons, lampblack 23,000 tons and acetylene black 7,000 tons.

In the first eleven months of 1955, the total U.S. carbon black shipment was 1.7 billion pounds while the stock inventory was about 218 million pounds. (27) The Free World consumption of carbon black in 1956, was estimated to be 2 billion pounds.

According to U.S. Bureau of Mines, the total U.S. carbon black production in 1957 was 1.8 billion pounds (594,065,000 in 1941) (28) and the general consumption pattern of carbon black was 1.5 billion pounds by rubber industry, 45 million pounds by ink industry and 13.5 million pounds by paint industry.

There are five principal factors which stimulate the growth of carbon black markets:

- 1 - The increasing per capita use of motor transport throughout the world.
- 2 - Higher speeds of motor vehicles.
- 3 - Greater horsepower of motor vehicles.
- 4 - Extensive utilization of rubber in mechanical goods.
- 5 - The highway program. The Free World outside the United States is increasing its rubber consumption.





### III DISCUSSION OF THE PRINCIPLE OF VARIOUS PROCESSES FOR MANUFACTURING CARBON BLACK

#### 1. Channel Process.

The principle of the channel process is to impinge the diffusion flame of unconfined partial combustion of natural gas on an air-cooled or a water-cooled metal surface which is called the "channel". There is no air pre-mixed with the feed gas. The necessary amount of air for burning the gas is controlled by natural drafts from the bottom and the top of each burner house. The carbon black once formed is exposed to air at temperatures high enough for appreciable surface oxidation to occur on the exposed carbon black. The characteristic properties of channel black are as follows:

- a) low PH
- b) a high volatile content
- c) a less chainlike structure between particles
- d) excellent reinforcing properties in natural rubber.

The most serious drawback of the channel process is its low yield. For 1000 s.c.f. natural gas the maximum yield is 2.5 lbs. of channel black. The average yield of channel process in 1950 was 1.75 lbs. of channel black per 1000 s.c.f. of natural gas. The production of channel black has been declining steadily.

#### 2. The furnace thermal process (conventionally, it is simply called thermal process).

The principle of this process is the regenerative cracking of natural gas or liquid hydrocarbon vapor into carbon black and hydrogen by heat





transferred to the gas or the vapour, from the refractory surface of a checker work of firebrick which has been cyclicly preheated to 2200-3000°F by the complete combustion of a mixture of natural gas and air. The characteristics of this process are:

- a) no oxygen is present during the cracking of the feed gas or feed vapour.
- b) the yield is considerably higher. The maximum yield is up to 16 lbs. per 1000 s.c.f. of natural gas.
- c) the hydrogen produced from cracking can be used in the synthesis of ammonia, as a fuel, or as a diluent of the feed gas in the furnace thermal process to modify the properties of the carbon black produced.

The carbon black produced by this process is simply called thermal black which has coarser particles and inferior reinforcing property.

### 3. Furnace combustion process (conventionally, it is simply called furnace process).

The principle of furnace process is partial and confined combustion of carbon-containing gas or vapour under closely controlled high-turbulence conditions. The carbon black once formed is not exposed to an oxygen-containing atmosphere. There are two types of furnace processes:

- a) gas furnace process. In this process, natural gas is used as the principal raw material (29). It may be enriched with higher hydrocarbon to increase the carbon content (30). This process is a continuous one and works on the same basic principle as that of the channel process except that





it does not employ either impingement or small flames. The gas and air are introduced into the furnace chamber in such a way that there is as little intermixing as possible; and therefore only partial combustion can take place between the gas and air layers. The partial burning of the hydrocarbons creates sufficient heat to decompose the rest of the hydrocarbons into black and gaseous products. The carbon black produced is called gas furnace black which has a particle size intermediate between channel blacks and thermal blacks. It was once in great demand for use in compounding synthetic rubber, because it permitted high loadings with low heat generation and still maintained good elasticity and rebound characteristics. However the rush for gas furnace black is already over, and the production is down.

b) oil furnace process. The production of carbon black by the oil furnace process is on a rising trend. It is predicted that by 1975, 80% of U.S. carbon black production will be from oil by furnace process (31). Therefore, this process deserves to be discussed in detail.

The principle of this process is the confined partial combustion of liquid hydrocarbons under conditions of high turbulence. The carbon black once formed is not exposed to an oxygen-containing atmosphere. It is believed that, in the oil furnace process, carbon black is formed only by the condensation or aggregation of molecular fragments existing momentarily in the products of cracking from the vaporized hydrocarbons in a flame front (32). In other words, the liquid hydrocarbons must be vaporized first before the cracking. If the liquid raw materials are still in the form of droplets during the cracking, "coke balls", instead of carbon black, are formed.



In the Ayers patent (33) the introduction of tangential air into the furnace and the use of atomized oil as a feed stock were first mentioned. Among the various modifications (34) the tangential introduction of a mixture of gas and air in a precombustion step as a source of heat was most significant.

The tangential introduction of the gas mixture gives a whirling gas mass which will cling to the side of the reactor and leaves a hot hollow core through which the vaporized oil can pass. Moreover, the deposition of the carbon black on the wall of the reactor can thus be avoided. The temperature of the furnace is maintained at less than 2600°F by controlling the air supply (30).

There are eight principal steps in oil furnace process:

First, feed preparation:	Including blending, preheating, filtering desulfurizing, dehydration, precracking, compressing for gaseous fuels, and vaporizing and pressuring for liquid fuels.
Second, Combustion:	This step includes the vital atomization of the hydrocarbons, unless vaporized oil is used. Together with the exact control of the turbulence of the gas mass, and the relative positions of the atomized fuel (the make fuel), the heating fuel (the auxiliary fuel) and air stream, the combustion step constitutes the heart of the process.





- Third, Cooling: Including the quenching of the reaction products, and the final adjustment of the temperature to protect the collecting system.
- Fourth, Primary collection: Collecting the bulk of the carbon black produced
- Fifth, Secondary collection: Being the final cleaning-up necessary to avoid any air and water pollution caused by smoke or sludge.
- Sixth, Processing: Densifying and dry pelletizing or wet pelletizing (followed by drying), to save space during transportation and to eliminate dust nuisance.
- Seventh, Product control: Including tests in various rubber compounds or ink formulations depending upon the end use.
- Eighth, Packing and shipping: Including the handling of bulk pelletizing carbon black.

Aromaticity is the most important property of a liquid hydrocarbon used in the manufacture of carbon black in oil furnace process. Aromatic hydrocarbons, such as benzene, not only give a higher yield of carbon black but also give a more finely divided black, and a characteristic higher degree of agglomeration of particles, which is usually referred to as "structure" of the carbon black. If polynuclear aromatic hydrocarbon, such as anthracene, is used as the raw material, the yield, the fineness, and the degree of agglomeration of the resulted carbon black are all accentuated to a higher degree. A desirable raw material is a mixture of di-tri- and polynuclear





aromatic hydrocarbons substantially free from asphaltenes and low in resins.

Today there are 3 main types of liquid hydrocarbons used in the oil furnace process for the manufacturing of carbon black.

- 1) cyclic stocks from catalytic and thermal cracking
- 2) aromatic extracts from catalytic stocks
- 3) tar from thermal cracking of catalytic cycle stocks.

Liquid hydrocarbons from coal tar, such as anthracene oil, are used commercially in oil furnace process only in England and Germany.

Although the amounts of liquid hydrocarbons required in oil furnace process represent only a very small fraction of total petroleum production, stable and adequate supplies of those liquid hydrocarbons of uniform quality are not easy to obtain. The oil industries have not made use of those liquid hydrocarbons, but they are trying to extract the aromatics out of those stocks, which would make the residue less suitable for oil black furnaces. Moreover, the tendency to substitute catalytic cracking for thermal cracking, and the decrease of heavier aromatics due to coking operation, both seriously affect the aromatic feed supply for use in oil furnace process. Coal tar fraction or oil from synthetic fuel plants can be used readily in the oil furnace process whenever economic factors justify such shifts.

The carbon black produced by the oil furnace process is conventionally called oil black, which has an average diameter of about  $34 \text{ m.u.}$  and contains large quantities of absorbed air and gases. In fact, the particle size of oil black can be controlled over a wide range. Rubber stocks containing oil black generally may be vulcanized faster than stocks containing channel blacks, but with proper adjustment of accelerators and





other compounding ingredients, the outstanding reinforcing and abrasion-resistant properties of channel black can be obtained without undue processing difficulties. Although oil blacks are especially suitable for compounding the synthetic rubber, they are also used for compounding with natural rubber. In addition, H A F (high abrasive furnace) oil black imparts an even higher resistance to abrasion in a rubber stock than does channel black.

#### 4. The autothermic process used in this research.

The general feature of the various processes for the manufacture of carbon black is that a large amount of heat must be supplied during the cracking of the hydrocarbon feeds. In the thermal process, the required heat is regeneratively supplied. In the channel process and in the furnace process, the required heat is internally supplied by the combustion of a part of the hydrocarbon feed. Since the combustion takes place in a large excess of hydrocarbon and in a reducing atmosphere, the combustion of the fuel hydrocarbon will be incomplete. Therefore, the fuel economy in processes mentioned above will be low.

In this process, the fuel gas (i.e. the natural gas) and the air with/without the additional oxygen were stoichiometrically premixed. As the mixture of the gas passed through the holes of the very hot surface of the burner or combustor, a complete combustion of the fuel gas was obtained. The heat of complete combustion was used in turn to crack the atomized hydrocarbon feed. Consequently, a better fuel economy was achieved. It was assumed that the combined effect of quick quenching and short retention time would not allow the endothermic "reforming" reaction between hydrocarbon



and water vapour to proceed to any appreciable extent. The reasonable success of this process substantiated this assumption. Another advantage of this process is that the deposition of carbon black on the walls of the furnace (generally a serious problem in carbon black manufacturing) did not occur in this process.





THERMOCHEMICAL REACTION  
FOR THE  
MANUFACTURING OF CARBON BLACK

The basic principle for the manufacture of carbon black is to crack, at the temperature range of 2000-3000°F, a gaseous hydrocarbon, the vapour of a liquid hydrocarbon, or an atomized liquid hydrocarbon into hydrogen and carbon. The physical state of the carbon formed depends upon the operating conditions. However, among all the major industrial processes for the manufacture of the carbon black, only the thermal process, can be considered as a true pyrolysis reaction, while the side-reactions of the other industrial processes are so pronounced that sometimes the pyrolytic nature of the various processes are overshadowed by the side-reactions. Furthermore, the simultaneous side-reactions at high temperature among the carbon, hydrogen, carbon dioxide, carbon monoxide, water vapour, and the vapour of the hydrocarbons are so complicated that practically no theoretical discussion or treatment, which has been generally accepted, can be found in the textbook or in the published literature. Nevertheless a general and thermalchemical consideration may lead to a qualitative understanding of the processes for the manufacture of the carbon black.

The free energy of formation of some gaseous hydrocarbons from the graphite and the hydrogen gas can be calculated from the following formulas (62) with reasonable accuracy:

$$\text{For } \text{CH}_4, \Delta F(\text{g. cal./g.mol.}) = -21,470 + 26.0T \text{ (}^\circ\text{K)}$$

$$\text{For } \text{C}_2\text{H}_6, \Delta F(\text{g. cal./g.mol.}) = -24,900 + 51.0T \text{ (}^\circ\text{K)}$$

$$\text{For } \text{C}_n\text{H}_{2n+2}, \Delta F(\text{g. cal./g. mol.}) = -11,260 + (n)6440 + (n)25.6T \text{ (}^\circ\text{K)}; n \geq 4$$



For benzene,  $\Delta F(\text{g. cal./g. mol.}) = 17,200 + 43.0T$

∴ at  $2200^{\circ}\text{F}$  ( $1478^{\circ}\text{K}$ ),  $(\Delta F)_{\text{CH}_4} = -21,470 + 38,400 = 16,930 \text{ g.cal./g. mol.}$

$$(\Delta F)_{\text{C}_2\text{H}_6} = -24,900 + 75,300 = 50,400 \text{ g. cal./g. mol.}$$

$$(\Delta F)_{\text{benzene}} = 17,200 + 63,500 = 80,700 \text{ g.cal./g. mol.}$$

Diesel oil consists of  $\text{C}_{10}$  -  $\text{C}_{18}$  normal paraffins with a small portion of olefins; hence it may be considered to be a normal paraffin with an average of 15 carbon atoms.

Therefore,  $(\Delta F)_{\text{diesel}} = -11,260 + 96,600 + 568,000 = 653,340 \text{ g. cal./g. mol.}$  For the purpose of comparison, the free energies of formation per carbon atom are calculated:

$$(\Delta F)_{\text{CH}_4}/\text{carbon atom} = 16,930 \text{ g. cal./carbon atom}$$

$$(\Delta F)_{\text{C}_2\text{H}_6}/\text{carbon atom} = 25,200 \text{ g. cal./carbon atom}$$

$$(\Delta F)_{\text{benzene}}/\text{carbon atom} = 13,450 \text{ g. cal./carbon atom}$$

$$(\Delta F)_{\text{diesel}}/\text{carbon atom} = 43,500 \text{ g. cal./carbon atom}$$

Let free energy of decomposition  $(\Delta F)_d = -(\Delta F)$

Then, the calculated free energy of decomposition per carbon atom at  $2200^{\circ}\text{F}$  will be:

$$(\Delta F)_d \text{ for } \text{CH}_4 = -16,930 \text{ g. cal./carbon atom}$$

$$(\Delta F)_d \text{ for } \text{C}_2\text{H}_6 = -25,200 \text{ g. cal./carbon atom}$$

$$(\Delta F)_d \text{ for benzene} = -13,450 \text{ g. cal./carbon atom}$$

$$(\Delta F)_d \text{ for diesel} = -43,500 \text{ g. cal./carbon atom}$$

Therefore, at  $2200^{\circ}\text{F}$ , diesel oil is easier to be cracked into carbon and hydrogen than natural gas which consists mainly of methane. In general, hydrocarbons of high carbon-to-hydrogen ratio are better raw materials for the manufacture of carbon black than those of low carbon-to-hydrogen ratio.





In industry, cracking is referred to the heat treatment of the hydrocarbons in the temperature range of 660-1200°F (350-650°C), while pyrolysis is related to heat treatment of the hydrocarbons above 1200°F.

The heat of decomposition (= -heat of formation, B.T.U./lb.mole)

of CH<sub>4</sub> at 2200°F,  $(-\Delta H)_{\text{CH}_4}^{1478^\circ\text{F}}$ ,

$$\begin{aligned} &= (-\Delta H)_{\text{CH}_4}^{298^\circ\text{K}} + \int_{298^\circ\text{K}}^{1478^\circ\text{K}} (C_{pC}) dT + 2 \int_{298^\circ\text{K}}^{1478^\circ\text{K}} (C_{pH_2}) dT - \int_{298^\circ\text{K}}^{1478^\circ\text{K}} (C_{pCH_4}) dT \\ &= (-\Delta H)_{\text{CH}_4}^{298^\circ\text{K}} + (\Delta H_C)_{298^\circ\text{K}}^{1478^\circ\text{K}} + 2(\Delta H_{H_2})_{298^\circ\text{K}}^{1478^\circ\text{K}} - (\Delta H_{\text{CH}_4})_{298^\circ\text{K}}^{1478^\circ\text{K}} \\ &= 32,300 + 9,800 + 2 \times 15,000 - (-32,300 - 500) \\ &= 105,000 \text{ B.T.U./lb. mole (or per lb. atomic wt. of carbon)} \end{aligned}$$

Similarly, the heat of decomposition of benzene at 2200°F,

$$\begin{aligned} &= (-\Delta H)_{\text{C}_6\text{H}_6}^{298^\circ\text{K}} + 6(\Delta H_C)_{298^\circ\text{K}}^{1478^\circ\text{K}} + 3(\Delta H_{H_2})_{298^\circ\text{K}}^{1478^\circ\text{K}} - (\Delta H_{\text{C}_6\text{H}_6})_{298^\circ\text{K}}^{1478^\circ\text{K}} \\ &= -36,100 + 6 \times 9,800 + 3 \times 15,000 - (130,500 - 36,100) \\ &= -26,700 \text{ B.T.U./lb. mole (or -4,450 B.T.U./lb. atomic wt. of carbon).} \end{aligned}$$

The heat of decomposition of diesel oil (C<sub>15</sub>H<sub>32</sub>) at 2200°F,

$$\begin{aligned} &= \text{heat of decomposition at } 77^\circ\text{F} + (\Delta H_C)_{298^\circ\text{K}}^{1478^\circ\text{K}} + \frac{16}{15} (\Delta H_{H_2})_{298^\circ\text{K}}^{1478^\circ\text{K}} \\ &= \frac{(680)(7.6)(12)}{(6.6)} + 9,800 + \left(\frac{16}{15}\right) (15,000) = 35,200 \text{ B.T.U./lb. at. wt. carbon.} \end{aligned}$$

Therefore, at 2200°F, the cracking of methane is strongly endothermic, the cracking of diesel oil is much less endothermic while the cracking of benzene is actually exothermic. Obviously from the viewpoint of heat requirements, of the three, benzene is the best raw material for making carbon black.





Three types of reaction can occur during the cracking or pyrolysis.



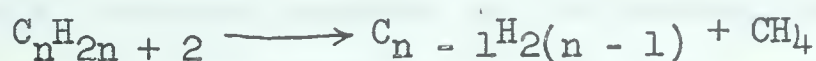
3. ultimate chain rupture and dehydrogenation:



From the standpoint of the manufacture of carbon black, the ultimate dehydrogenation and chain-rupture reactions of the hydrocarbons are of special interest and importance.

The energy required to rupture a C-C link is about 80 K cal./mol., and that for C-H link is about 100 K cal./mol. (63). Generally speaking, the breaking of a C-C link requires some 20 K cal./mol. less energy than the breaking of a C-H link. However, for ethane and isobutane, the dehydrogenation takes place more readily than the chain-rupture reaction during the pyrolysis (64). Therefore, except the cases of ethane and isobutane, under non-catalytic conditions, the velocity of the reaction of the chain rupture should be greater than the velocity of the dehydrogenation reaction.

According to the Haber's rule of cracking, when two molecules are formed from the cleavage of a paraffin, the smaller one should be a paraffin molecule, while the larger one should be an olefinic molecule. Due to the abnormal stability of methane, the de-methanation and, to lesser extent, the de-ethanation are best favoured, in the chain rupture reaction on the thermodynamic grounds, i.e.,







This conclusion finds some support from the presence of methane as one of the major constituents of the gases from the ordinary cracking process.

There are four kinds of bonds between carbon-and-carbon and between carbon-and-hydrogen, which are of special interest in connection with the pyrolysis.

1. C-C bond, 80 K cal./mol.
2. C-H bond, 100 K cal./mol.
3. C=C bond, 145 K cal./mol.
4. C≡C bond, 198 K cal./mol.

The bond energy figures indicate that it requires more energy to crack the double bond between two carbon atoms than to crack the single bond between two carbon atoms. However, the prevailing opinion and experience in the carbon black industry is that aromatic hydrocarbons (unsaturated ring compounds) are easier to be cracked into the carbon black than the aliphatic hydrocarbons, and require less amount of the fuel for the cracking. In this research, when benzene was injected into the furnace, the temperature of the reaction zone slightly went up instead of going down as it was in the case when the diesel oil was injected into the furnace. This showed that some energy was evolved.

During the pyrolysis, if the temperature is high enough, and if enough quantity of heat is supplied, theoretically the ultimate chain-rupture and dehydrogenation can be obtained. However, due to side reactions at the high temperature, only a certain fraction of the hydrocarbon introduced will be ultimately cracked into carbon black, even if the cracking is followed by very efficient quenching. The most serious side reactions may probably be as



follows:

1. the water gas reaction,  $C + H_2O \longrightarrow CO + H_2$
2. the reform reaction,  $CH_4(\text{hydrocarbon}) + H_2O \longrightarrow CO + 3H_2$
3.  $C + CO_2 \longrightarrow 2CO$

These side reactions will either consume a part of the hydrocarbon feed, or a part of the carbon black produced from the pyrolysis. Consequently, the overall conversion of the carbon in the hydrocarbon feed into carbon black by the existing processes for the manufacture of the carbon black can hardly exceed 60%. If the temperature for the manufacture of the carbon black is raised above the optimum temperature, the yield of the carbon black starts to drop sharply. This can be qualitatively explained that higher temperature will favour and accelerate all the three side reactions mentioned above, since they are all endothermic reactions. However, the complete and true mechanism of all the simultaneous side reactions are so complicated that very little information has been published in the literature. Therefore, no quantitative investigation about the effect of the side reaction in the production of the carbon black was attempted in this research.





#### IV THE SCIENTIFIC VARIABLES DETERMINING THE YIELD AND QUALITY OF CARBON BLACK

##### 1. Air-gas (or oil vapour) ratio:

Air-gas ratio determines the temperature of the furnace, and has an important bearing on the yield and properties of the carbon blacks produced. Under normal operating conditions, the yield of carbon black increases as the temperature rises to about  $2200^{\circ} - 2400^{\circ}\text{F}$ ,<sup>(30)</sup> and then falls off with further increase in temperature. The resinous polymerized hydrocarbons decrease continuously with increasing temperature.

##### 2. Quality of carbon-bearing raw materials:

When nitrogen and oxygen in a fuel are in combined form and are in small amounts, they have no effect on the properties of the resulting carbon blacks. The combined form of sulfur in a fuel may show up as free and combined sulfur in the carbon blacks. The sulfur in the fuel gas is largely  $\text{H}_2\text{S}$  and perhaps partly in the form of  $\text{COS}$  <sup>(32)</sup>. For many years, fuels containing up to about 2.5% sulfur have been used to make carbon black for "fast extruding or smooth-out" and "higher abrasive" rubber. Free carbon in a fuel, either in the form of suspended thermal carbon black or in the form of coke particles, cannot be tolerated above a few tenths of 1%. Obviously the ash content of a fuel will show up as total ash content of the carbon black. Moreover, it will affect the life of furnace refractories, and the curing and aging characteristics of the rubber stocks compounded with the carbon black, largely due to traces of certain metals. Little is known about the effect of hydrogen<sup>(1)</sup>.



3. The pattern and velocity of flows of gas and air:

It was claimed that the pattern of flow, whether turbulent or streamlined, which was determined by the design of the burner (such as size, shape and number of air and gas inlets) was also important for the yield and quality of the carbon black. Moreover, a wide difference in gas and air velocities appears to favour the formation of chain-like agglomeration, while more nearly equal flowrates favour discrete particles.

4. Thickness of entering gas stream, and interface between entering air and gas:

It depends solely on the burner construction. When the thickness decreases and interface increases, both the particle size and the yield decreases (1).

5. Contact time:

It depends on the volume of air and gas, and on the furnace volume. Below a critical value of about 1/2 to 1 sec., the yield falls off sharply for temperatures around 2300°F. With decreasing contact time, extractable matter increases, and appreciable quantities of gas remain unreacted.

6. Aromaticity and carbon-hydrogen ratio of the fuel:

Aromaticity is the single most important property of a suitable carbon black fuel (32). It gives higher yield, more finely divided carbon black, and a characteristic higher degree of agglomeration of particles.





## V. SOME ADDITIONAL TECHNICAL VARIABLES IN CARBON BLACK PRODUCTION

The basic principle of the manufacturing of carbon black is very simple. Thermal cracking of hydrocarbons, whether by incomplete combustion or by some other heating devices, will invariably give high carbon content solids as one of the resulting products. Lamp black has been known for more than thousand years, but even today a great deal remains unknown about carbon black. Even when the solid particles from the thermal cracking of various hydrocarbons and by various processes, give the same ultimate analysis, these elemental carbons upon compounding with rubber, exhibit widely different performances. Thus, lamp black does not possess any reinforcing property when it is compounded in rubber. Even for carbon blacks, there are wide differences in degree of reinforcement, and other physical properties (such as plasticity, hardness, rebound, resilience, etc.) of the resulting rubber stock.

From the published literature and the patents of the manufacture of carbon black of various nations, some additional and technical variables which affect the quality and yield of carbon black are as follows:

1. preheating of the atomized or vaporized feed hydrocarbon and the fuel gas (35) (36) (37).
2. design, structure and plurality of burners of the fuel gas.
3. shape [cylindrical, (38) (39) rectangular or conical (40) (41) (42)], dimension (relative ratio of diameter to length) and construction of the reaction chamber.
4. operating pressure in the reaction chamber.



5. the method of introduction of the air or free oxygen containing gas (43) (44) (45) i.e., into the reaction zone (46), or into the pre-quenching zone.
6. the introduction of other gases, such as hydrogen, CO, (47) SO<sub>2</sub>, (48), nitrogen, CO<sub>2</sub> (3), or steam (51).
7. recycle of the flue gases (49) or wash oil containing some carbon black (50), into the reaction chamber.
8. number of stages of quenching, and the quenching temperature at each stage, and the mode of heat transfer during quenching, (i.e., direct or indirect contact with the coolant.)
9. quenching medium and its physical state, such as water spray, fog, fluidized bed, etc.
10. the mode of heat transfer in heating (i.e., direct, indirect, (52) radiant (53) (54) (55) or induction heating) (56); or any combination (35) of them.
11. the sources of heat required (i.e., heat from combustion of fuel-hydrocarbon, heat from combustion and pyrolysis of feed hydrocarbon, heat from some external source, or any combination of them) and the stage of their introduction. (57).





## VI. THE SCOPE OF THIS RESEARCH

One way of studying a complicated process, with so many inter-related variable operating conditions as those in the manufacture of carbon black, would be as follows:

1. studying the significance of each individual variable operating condition upon the properties of the final product.
2. then studying the significance of all the possible combinations of all the variable operating conditions upon the properties of the final products.

Such a procedure is obviously very tedious and expensive.

Consequently, research into carbon black production has been largely empirical. Indeed, comparatively few scientific articles about carbon black can be found in the literature. The largest source of the information for carbon black is found in the patents of various nations. In these patents there are hundreds of claims about the effect of combined effects of some of the supposedly important variables, such as flow pattern, the direction of injection of fuel gas, retention time, etc., which are believed to influence the yield and property of carbon black. Unfortunately, much of the information obtained from the patents is either contradictory or is so general that few definite conclusions can be drawn. Moreover, due to the expensive and complicated nature of the equipment and installation described in the patents, it is impractical to confirm all the results claimed.

The present investigation is to evaluate the surface combustion burner in a simple vertical reactor for the manufacture of carbon black from diesel oil and benzene, with particular interests in the quality and yield of the carbon black produced.



Diesel oil was chosen as the raw material for the production of carbon black in this research, because it is a reasonably cheap hydrocarbon which can be readily obtained from Alberta market. Moreover, it is easier to be cracked than natural gas. Some data from the result of a test run with benzene as the feed material was also included, in order to compare the cracking characteristics of the aromatic hydrocarbon and the properties of carbon black produced with those from diesel oil which is an aliphatic hydrocarbon.

The ranges of operating variables are as follows:--

diesel oil feedrate: 6-12 lb./hr; air flowrate: 13.01-20.55 scfm

natural gas flowrate: 1.49-1.98 scfm

oxygen flowrate: 0.452-0.918 scfm

space velocity, reaction zone: 5.4-7.4 ft./sec.

retention time: 0.14-0.19 second





## VII EQUIPMENT

### 1. THE DESIGN AND SELECTION OF BURNER

From both the literature and the patents, the temperature, design, construction, plurality, distribution, location of the burners, and the projecting direction of the burners are very important in the production of carbon black. Previous work had suggested the possibility of using some type of surface combustion burner <sup>(58)</sup>. Therefore a flameless surface combustion burner which can stand a temperature range of 2500-2800°F was chosen for this investigation. A Cox's Surface combustor had been used in previous pyrolysis studies but it was found that it could not stand the high temperatures required for carbon black formation. An attempt was to make a high temperature surface combustion burner from a stabilized zirconia plate. The dense type zirconia plate claims a top-use-temperature of 2500°C, but its poor permeability ruled it out in this case. Tests were carried out with a porous and insulating type of the stabilized zirconia plate, which claims a top-use-temperature of 2000°C. A plate, 10" x 6" x 1" was mounted and cemented to an iron casing with refractory cement. Air and natural gas were premixed through a proportional mixer (which is also called surface combustion inspirator) into the iron casing through an inlet hole. The gas mixture diffused to the surface of the zirconia plate. After ignition it burnt into a flameless incandescent surface. The self-made surface combustion burner performed satisfactorily when tested outside the furnace. When the burner was put to work in the furnace, it started to give all kinds of troubles. After several months of laborious and frustrating tests, this attempt to use a "home-made" surface





combustor was finally given up. Several types of high intensity radiant heat surface combustors, by Radiant Heating Ltd., were ordered and tried. The No. 4 type, which claims to give a surface temperature range of 1250-1450°C (with 100% gas/air mixture, up to 1600°C) and to release 2000-35,000 B.T.U. per square inch per hour, was chosen. This type of surface combustor worked satisfactorily through this research. The final size of the burner was determined by the rate of heat required to crack the liquid hydrocarbon feed.

After several preliminary test runs, there were indications that the first assumed cracking temperature of 2200°F was not high enough. Therefore, a bigger Radiant No. 4 type burner (having a heating surface of 12" x 6.5" and 45 outlet holes (3/4" I.D.) for the burning gas), which was composed of three smallest units (each having a heating surface of 4" x 6.5" and 15 holes for burning gas) was finally used. It gave satisfactory service throughout the rest of the research.

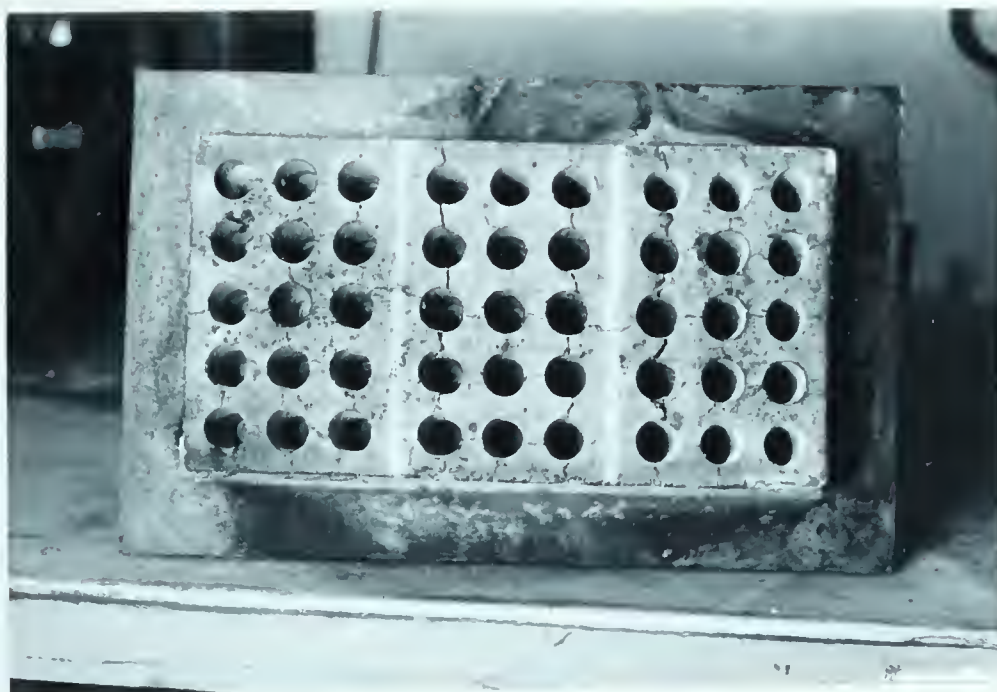


Fig. 1

No. 4 type radiant heat surface combustor,  
12" x 6-1/2". (hole 3/4" I.D.)





## 2. CHOICE OF FEED STOCK AND DESIGN OF ATOMIZER AND INJECTION MECHANISM

At present, a type of aromatic tarry residue produced from the thermal cracking of catalytic cyclic stocks of petroleum refinery is generally used as the feed for the oil blacks. Having a high carbon to hydrogen ratio it is easier to crack and gives excellent yields. However, due to its high viscosity and low volatility, it requires specially designed and expensive atomizer or burner, and is difficult to handle in the laboratory. Under the assumption that all hydrocarbons can be cracked into carbon black, No. 1 diesel oil was finally chosen as the raw material for the preliminary tests. The specifications were as follows:

API gravity = 36.7	; specific gravity = 0.841
Aniline point = 146°F	; 50% ASTM boiling point 490°F

After the raw material of feed had been decided, the immediate steps which followed were:

### 1. Selection of atomizer

Many types of spraying nozzle were under consideration in the start, but they were all ruled out one after another, due to either poor atomization or too large capacity. Finally it was decided to use the kind of injector found in General Motors diesel engine. This gave excellent atomization of diesel oil, but it gave six minute radial sprays of atomized diesel oil, with respect to the axis of the injector. This pattern of injection would have complicated the subsequent design of the reaction chamber, furnace, flow pattern of reacting gases, and the entire lay-out of the system. Consequently this was modified by replacing the radial



spray injector with a self-made spraying tip, made from stainless steel and machined exactly to match the old tip but with only one very small spraying hole drilled through its front end. The contact surface was given a mirror-finishing.

The specifications of the atomizer were as follows:

operating pressure of diesel oil = 40 psig

Capacity = approximately 2 U.S. gallons/hr. at 1750 strokes per minute, at full throttle.

## 2. Design of Injection System

This included the hold-fast, the insulation and cooling for the atomizer, the knocking mechanism, the lubricating, the weighing of diesel feed, and the coupling of the cam-shaft with the electric motor. All these were fairly simple mechanical works. When they were assembled together, it ran smoothly for short testing periods. Troubles started when the running time exceeded an hour. The real trouble was the coupling between the cam-shaft and the shaft of the electric motor, because the pad of the coupling could not stand the shock resulting from the cam-action at 1750 r.p.m. After about 2 months of laborious trial, the steelflex coupling, type F, by the Falk Corporation, was finally chosen. It performed smoothly through the rest of the research. Some specifications of the different parts of the injection mechanism are as follows:

Cam-shaft: 1750 r.p.m. ; striking arm of atomizer: 1750 strokes/min.  
pump for diesel oil: 3500 r.p.m.; diesel oil pressure: 40 psig.  
electric motor: 110 volts, 6.8 amp., 60 cycle, 1750 r.p.m., 1/2 H.P.





### 3. DESIGN OF REACTION CHAMBER AND FURNACE

The patent and technical literature showed wide variations in reaction chamber, flow pattern of fuel gases, location of burners, flow pattern and direction of make-gas etc. The reaction chamber may be cylindrical, rectangular or conical. The flow pattern may be highly turbulent, moderately turbulent, laminar or helical. The burner or burners may be at the up-stream and or down-stream end of the reaction chamber. The vapor of the hydrocarbon feed may flow with or against the stream of fuel gases. The reaction chamber may be horizontal or vertical, and may be open at both ends or only at one end. Its cross-sectional width may be smaller or bigger than its axial length. The gaseous product and carbon black suspension may go upward or downward through the reaction chamber.

Due to the shape and size of the surface combustion burners available, it was decided to make a reaction chamber with the following specifications:

1. the reaction chamber was rectangular with 6" x 6" square cross-section and a length of 46".
2. it is of the vertical type
3. only the bottom of the reaction chamber was open for the flow of the products.
4. one big burner of Radiant No. 4 type, which composed of 3 small burners of the same type, was put at the bottom wall of the reaction chamber, while the atomizer was located at the top dead-end.
5. the flow of the hot flue gas from the burner was perpendicular to that of the atomized diesel oil.
6. the dead space between the burner and the atomizer served to vaporize the diesel oil.



7. it was assumed that the expansion in volume of the vaporized diesel oil in the reaction chamber would give the gaseous products enough speed to flow through the chamber and the quenching section without any carbon black deposition on the walls. This assumption was justified from the results.
8. the refractory bricks (G-32, by A.P. Green Co.,) of the inner-most layer of the reaction chamber claimed to stand a temperature of 3200°F.
9. the reaction chamber and the fire bricks were confined and enforced by steel wall, bottom and cover made from 1/4 inch steel plate. The dimension of the furnace body was 28.5" x 16.5" x 41" with a rectangular top of 12" x 7" x 7".
10. the iron casing of the burner stuck out of the steel wall in order to get better cooling effect and to avoid back-firing.
11. all the injection mechanism and the electric motor sat on top of the steel cover.





## FIGURE 2 BODY OF REACTION FURNACE

Scale: 1 inch = 1 foot

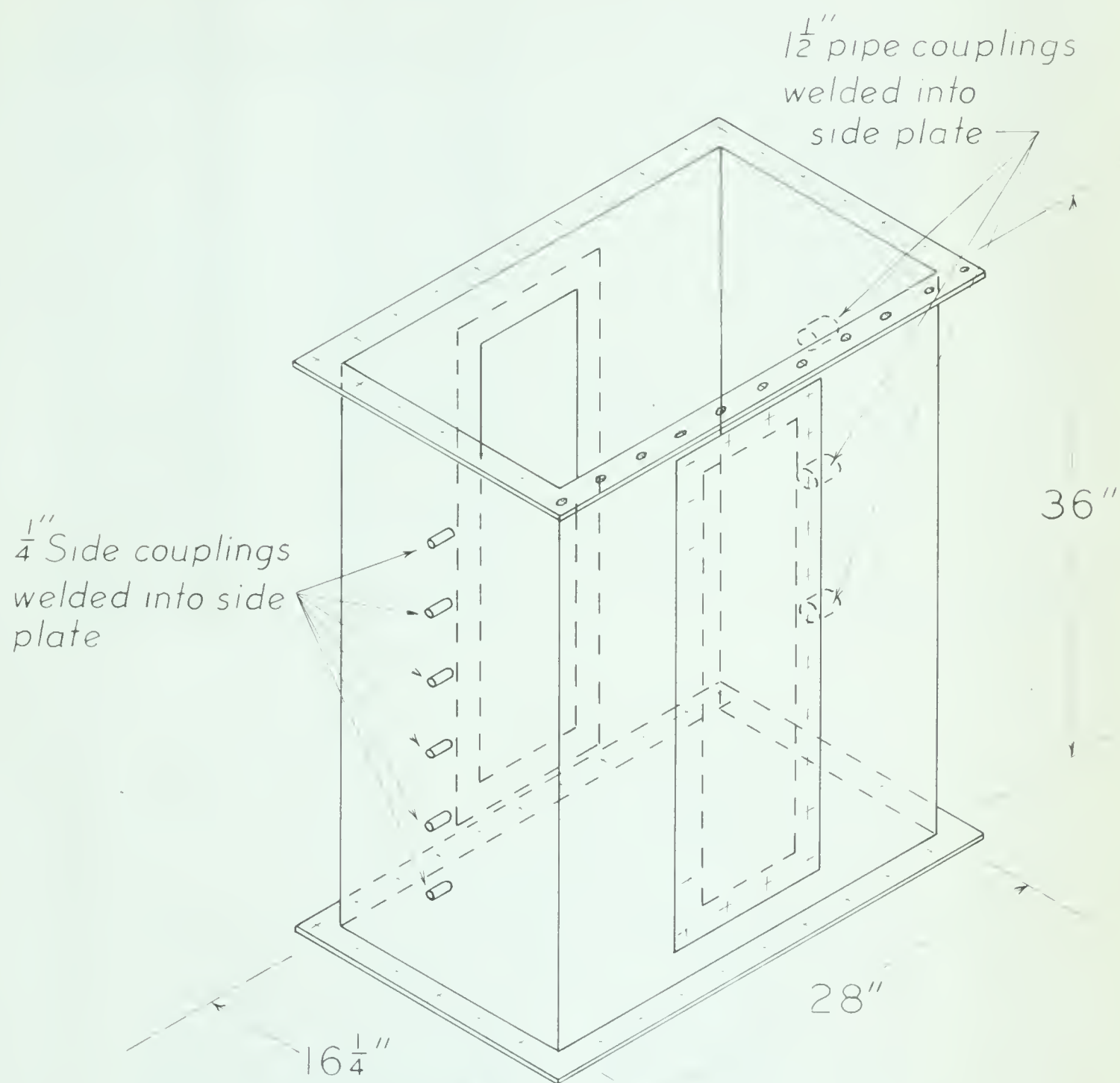




FIGURE 3  
REACTION FURNACE

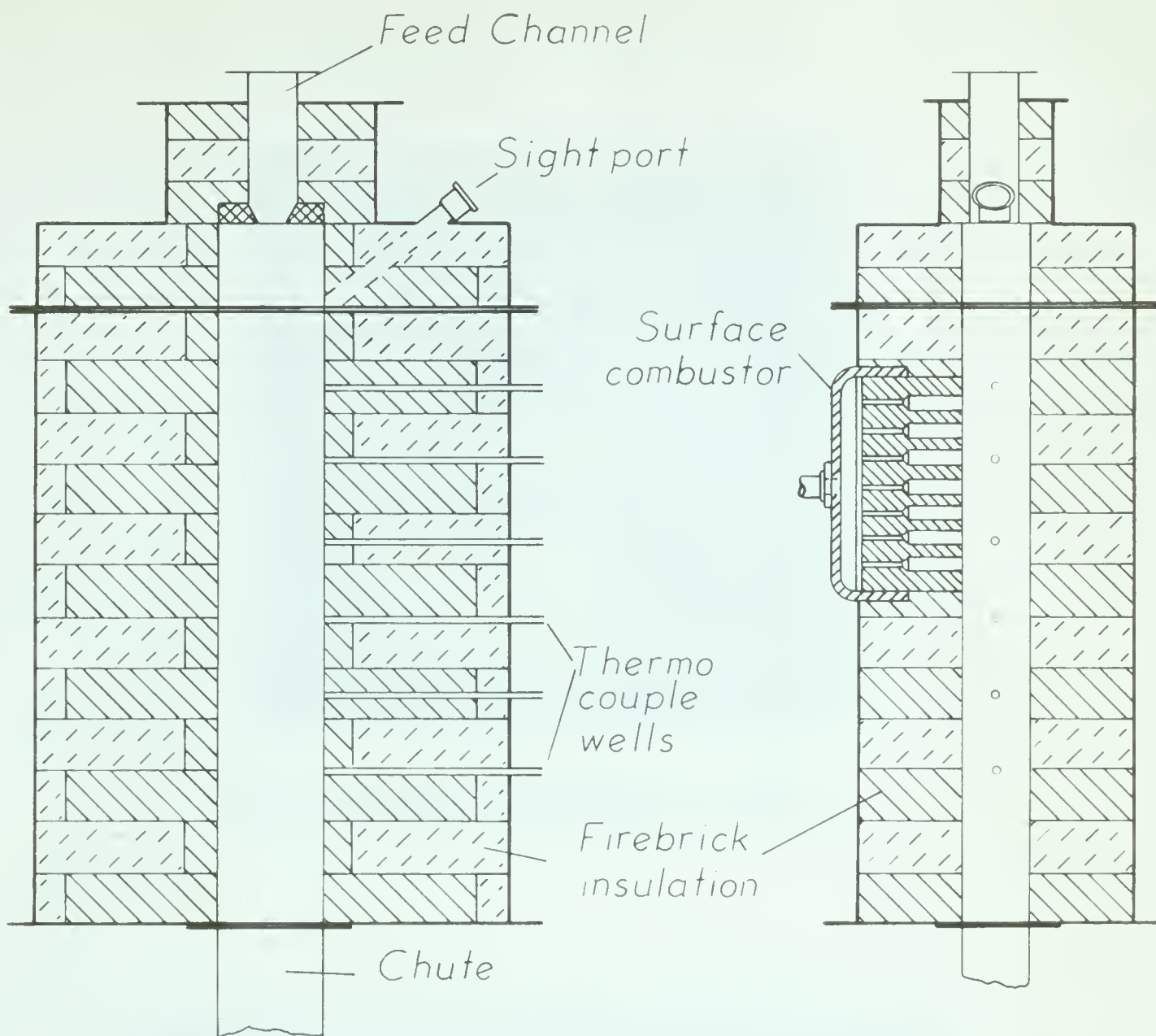
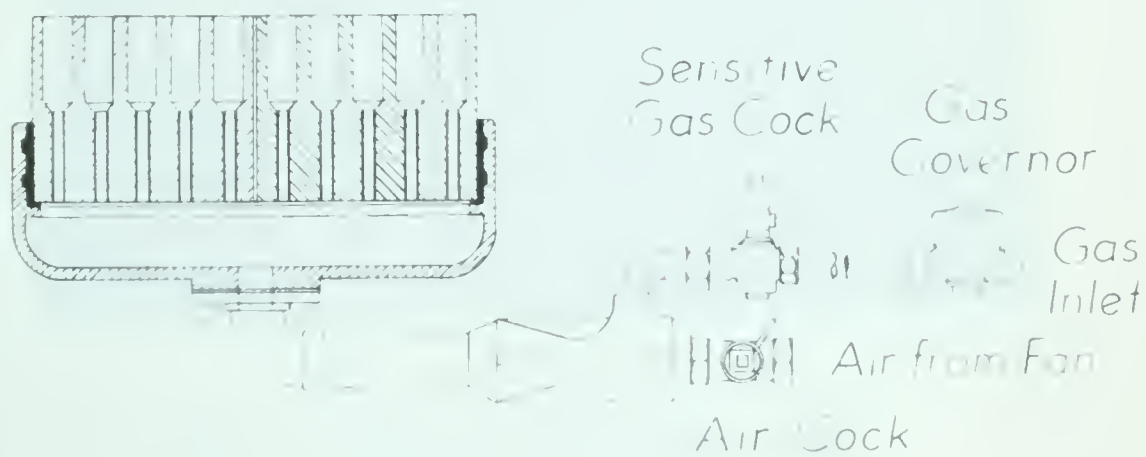


FIGURE 4  
REFRACTORY TUNNEL COMBUSTOR







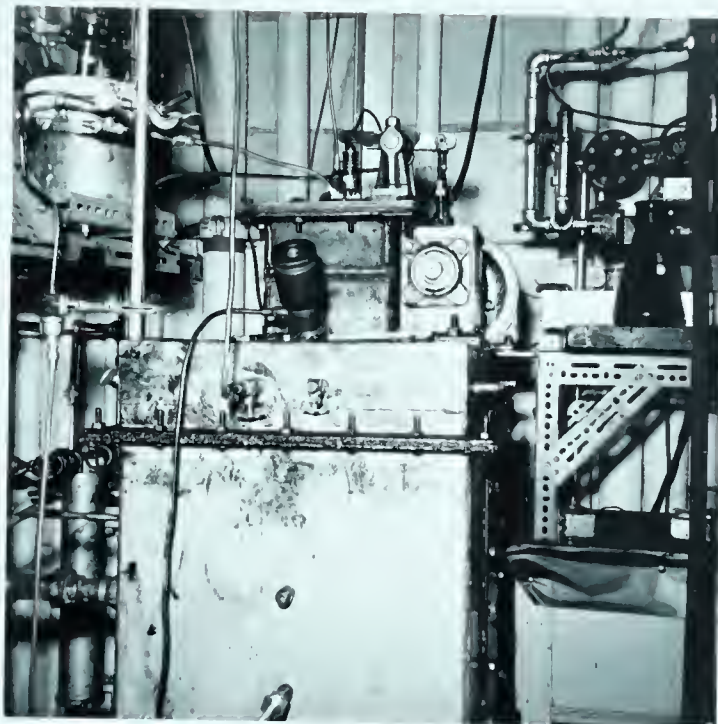


Fig. 5 Injector for diesel oil feed

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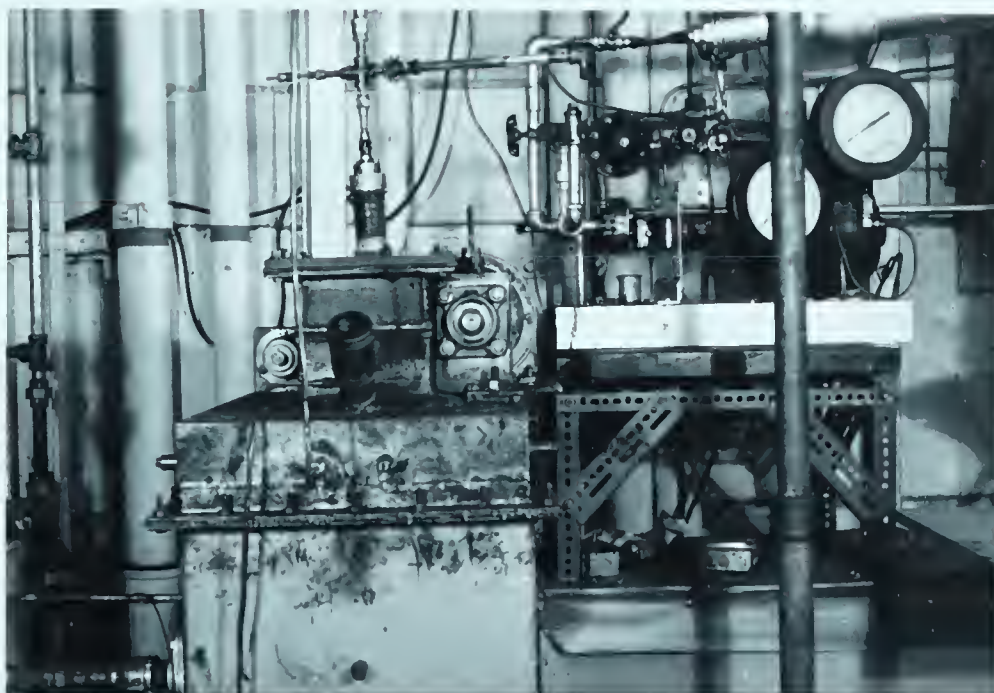


Fig. 6 Injector for benzene feed





Fig. 7. The steel wall of the furnace



Fig. 8. The burner inside the furnace





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Fig. 9. The burner and the reaction chamber

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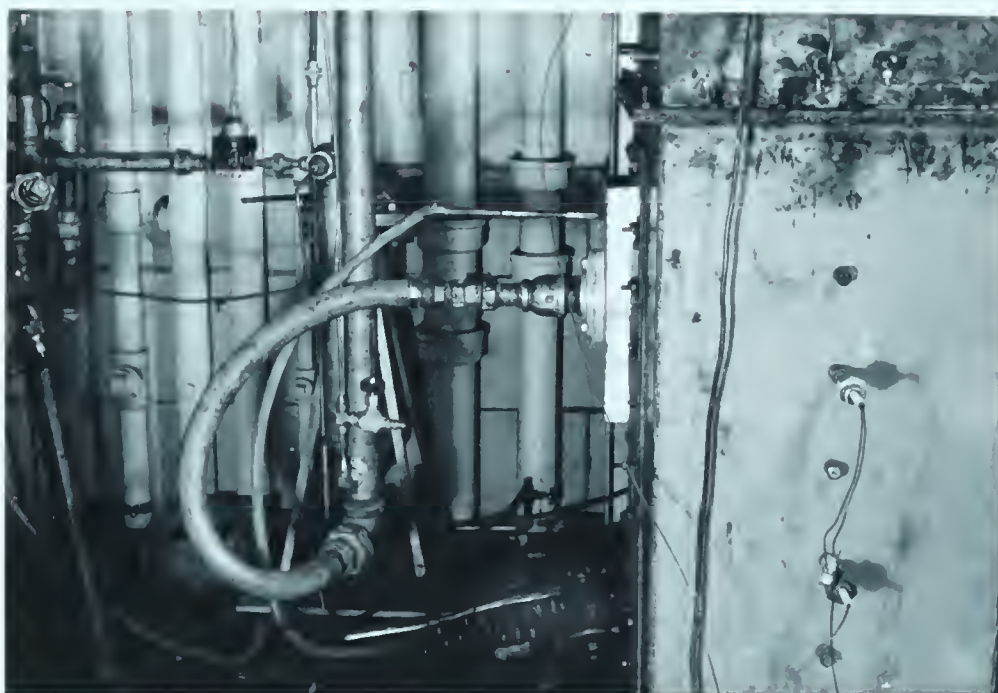


Fig. 10. The inlet and the iron casing of the burner



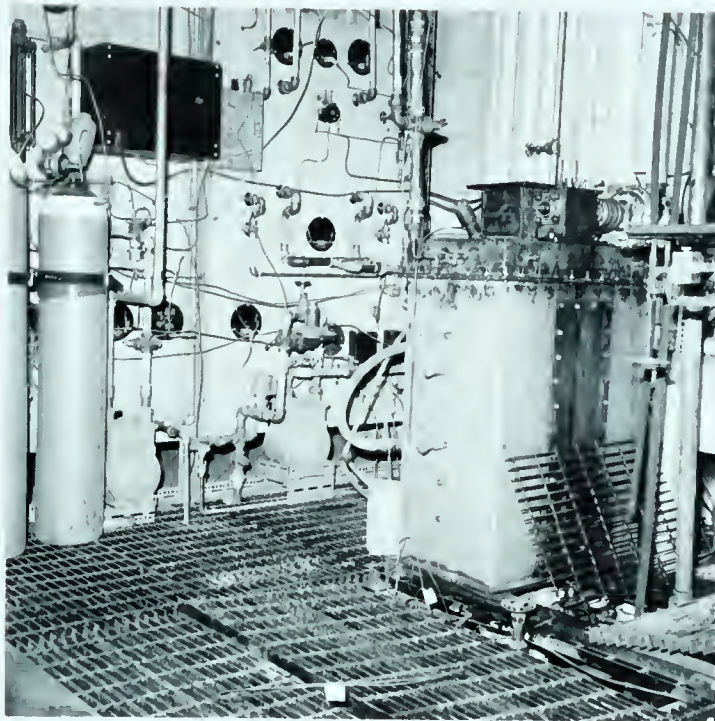


Fig. 11. The furnace and the back of the control board.

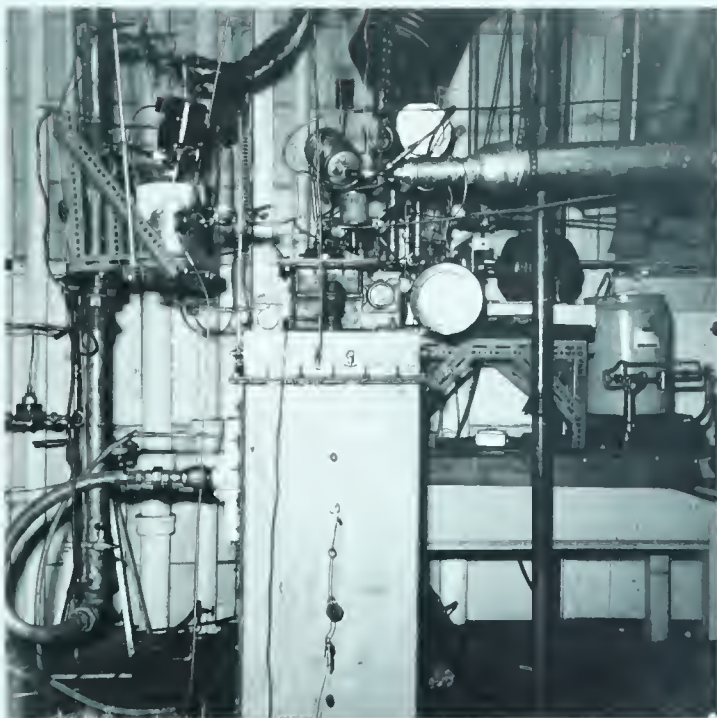


Fig. 12. The injection mechanism on the top of the furnace



Fig. 13. The injection mechanism





#### 4. THE QUENCHING MECHANISM

Industrially, the cooling is generally carried out in three steps. In the first step, the carbon black suspension is quenched with direct water spray to about 1000°F, then it is cooled by air to about 700°F by passing through a long pipe, and finally it is quenched again with water spray to about 300-500°F according to the heat resistant character of the final filtering medium. Due to the limited space in the research laboratory, only single stage cooling, by stainless steel spray nozzles, was adopted. The specifications of the nozzles are as follows:

Type M, male connection: Nozzle No. 1/4 M6: orifice diameter, 0.042"

Capacity (U.S. gal. per hr.) at various water pressures: at 25 p.s.i., 4.7:

at 30 p.s.i., 5.2: at 40 p.s.i., 6.0: at 60 p.s.i., 7.3

The city water was used as the quenching medium and the excess of the quenching water was drained to the sewer by intermittently opening the valve at the conical bottom of the primary carbon black collector.

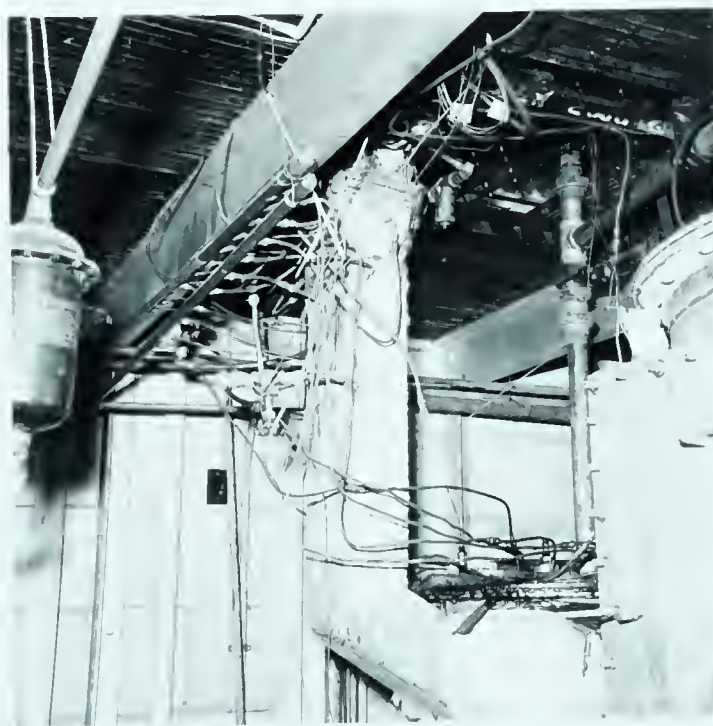


Fig. 14. The quenching section



## 5. THE COLLECTING SYSTEM

According to the published literatures and the patents, the collecting procedures for carbon black are generally as follows:

1. the quenched flue gas and the carbon black suspension are passed through a series of two or more cyclones. Thus, the bulk of the carbon black is removed.
2. the partially depleted gaseous suspension of carbon black is then passed through electrostatic Cottrell precipitator. However, the Cottrell precipitator can be avoided if more cyclones connected in series are used.
3. filtering bags made of orlon or fibre glass are used for the final stage collection of the carbon black. Practically all the carbon black is thus recovered from the flue gas which is vented to atmosphere through the stack, if it is not going to be recycled.

In this program, only a single stage collection of carbon black through filtering bags was adopted. At first, one filtering bag made of ordinary fibre glass was employed, but it did not stand the temperature, pressure and abrasion used in this research. After several months of frustrating effort in fighting against the breakage of the ordinary fibre-glass filtering bag, four silicone-treated<sup>(60)</sup> fibre-glass filtering bags, which were held in inverted position, were finally chosen. The gaseous suspension of carbon black passed into the inverted bags, and carbon black particles were retained on the inner wall of the filtering bag. When the pressure drop across the filtering bag was about 8-in of water, the injection of diesel oil was stopped, and the carbon black was shaken off the

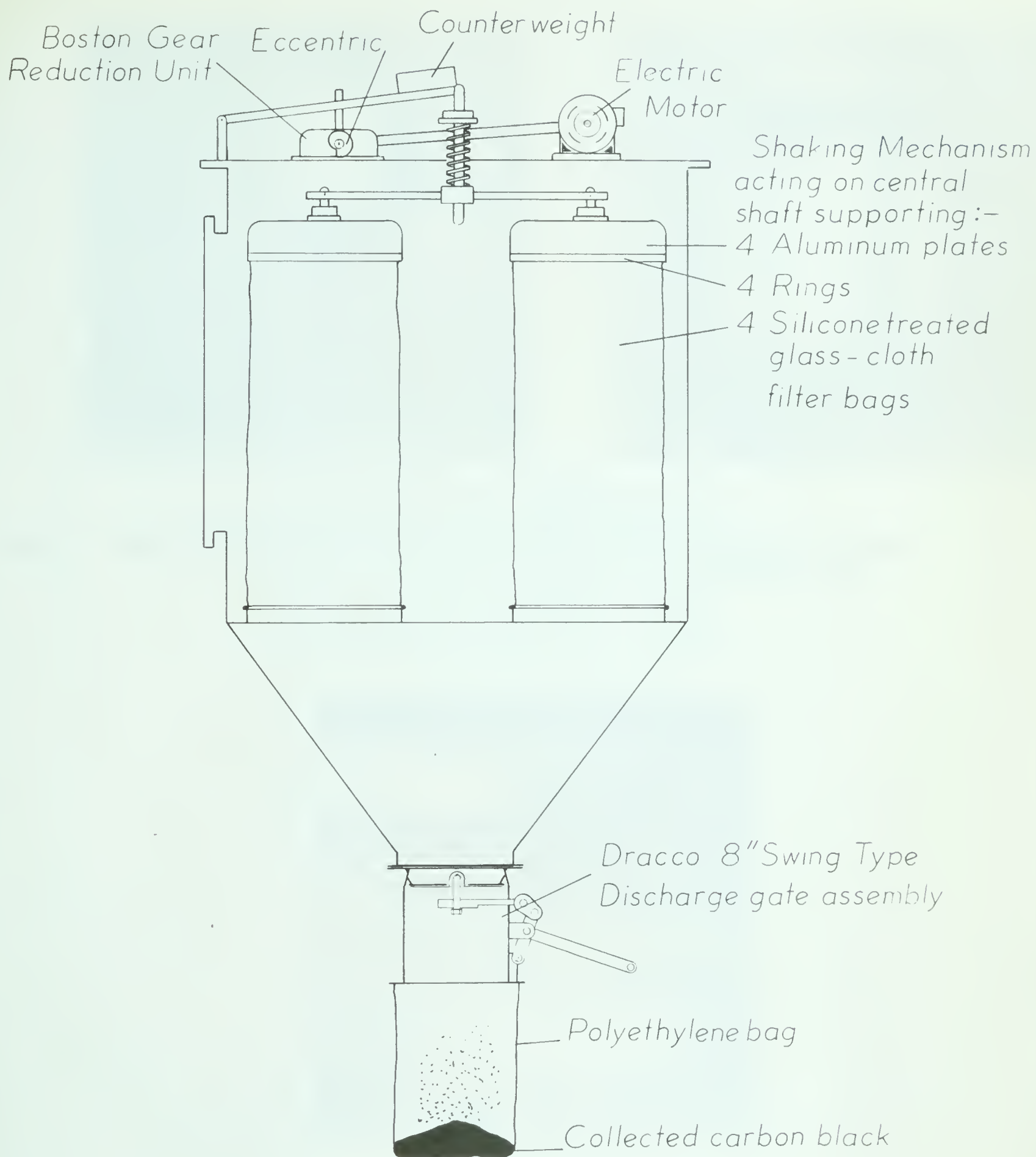




bags and into the bottom of the tank by a knocking mechanism on the cover of the collector. Through a "Dracco Swing gate valve," the carbon black was collected into polyethylene bags.



FIGURE 15  
CARBON BLACK COLLECTOR







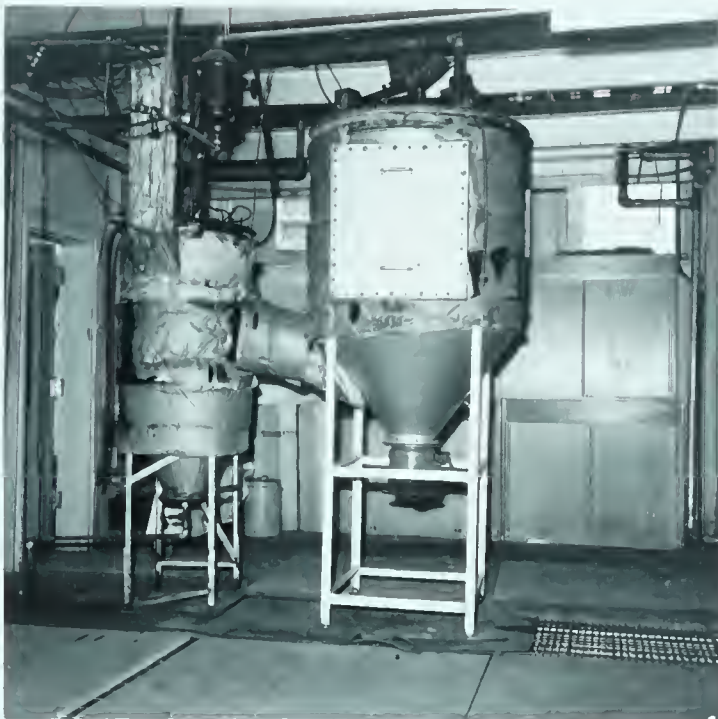


Fig. 16. The collecting Tank



Fig. 17. The silicone treated  
filtering bags

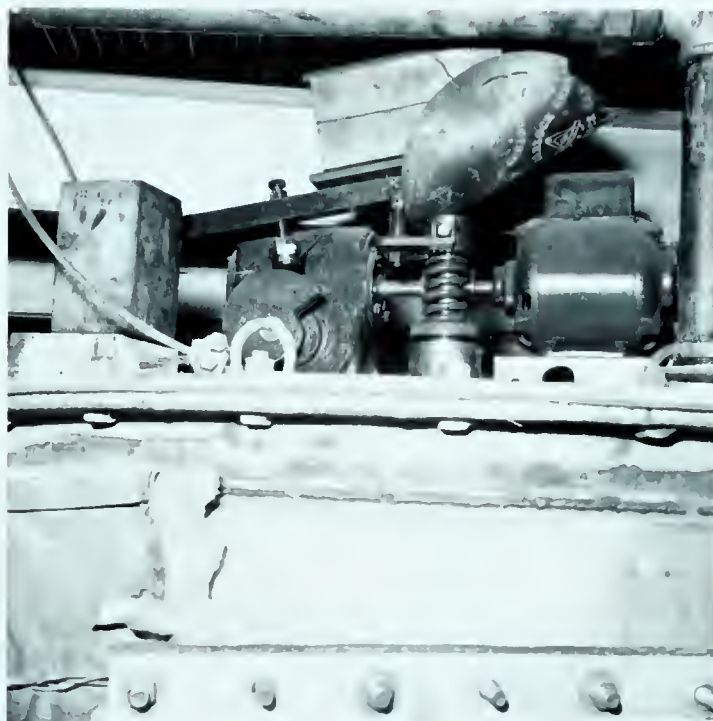


Fig. 18. The knocking mechanism on the cover of the collecting tank



## 6. THE PACKED COOLER

Before the filtered flue gas was measure in the gas meter, it was cooled countercurrently in a water-spray cooler which was 8" x 48" in height and packed with 3/4" Reschig rings. Meanwhile, the accompanying water vapour from the quenching zone was also condensed out.

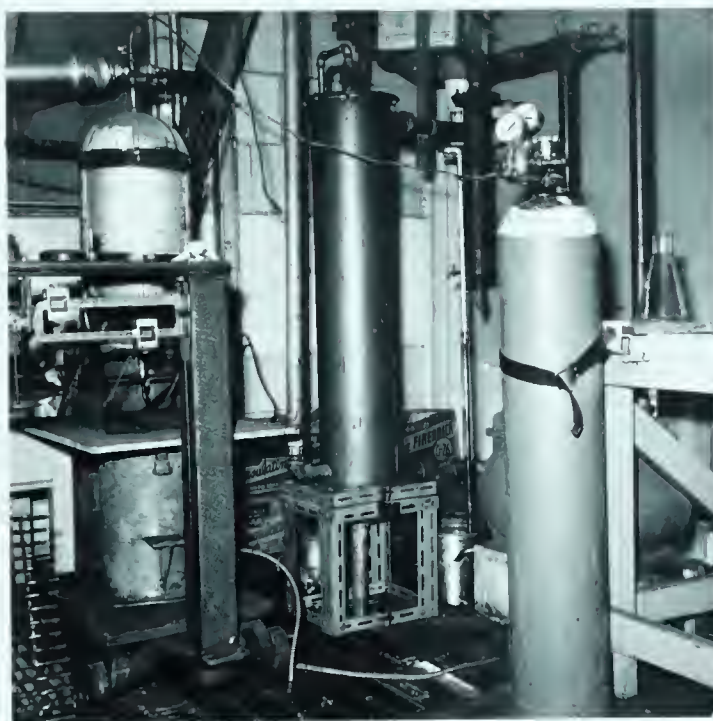


Fig. 19. The packed cooler





7. THE MEASURING AND QUALITY-CONTROLLING SYSTEM

The system mainly consisted of the following units:

1. A trap to remove the water particles carried over by the flue gas.
2. Two volumetric gas meters, each with a capacity of 900 cu. ft. per hour.

Before the flue gases entered the meters, their temperatures were measured by a thermometer, and their pressures by a manometer on the control board.

3. Collecting unit for gas sample
4. Beckman Oxygen analyzer Model F-3, Varian recorder, vacuum pump, etc.



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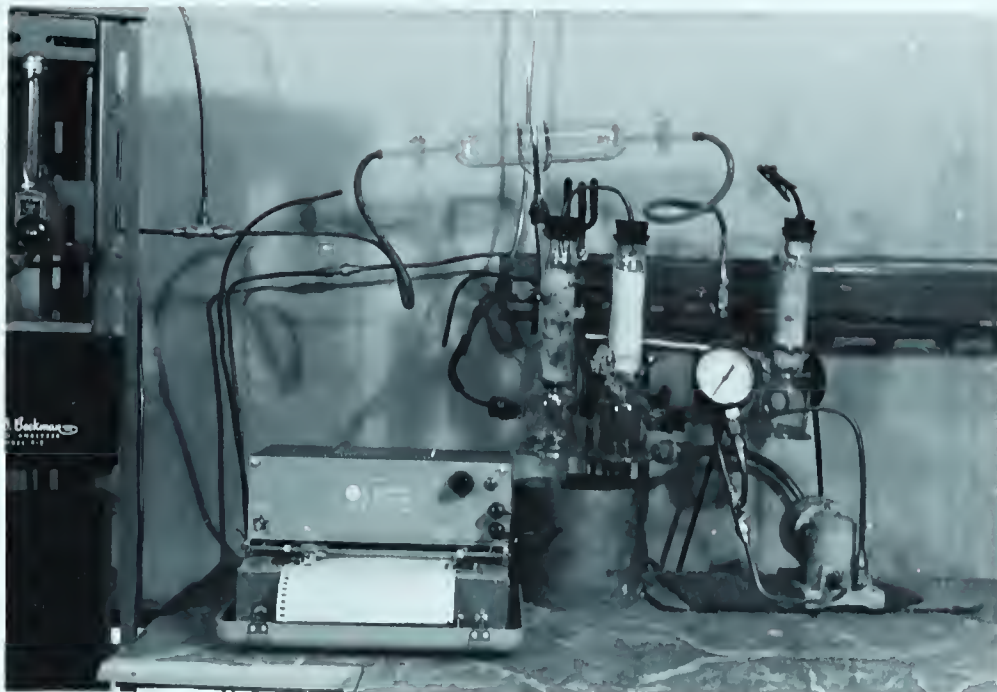


Fig. 20. The Varian recorder and the gas sampling unit

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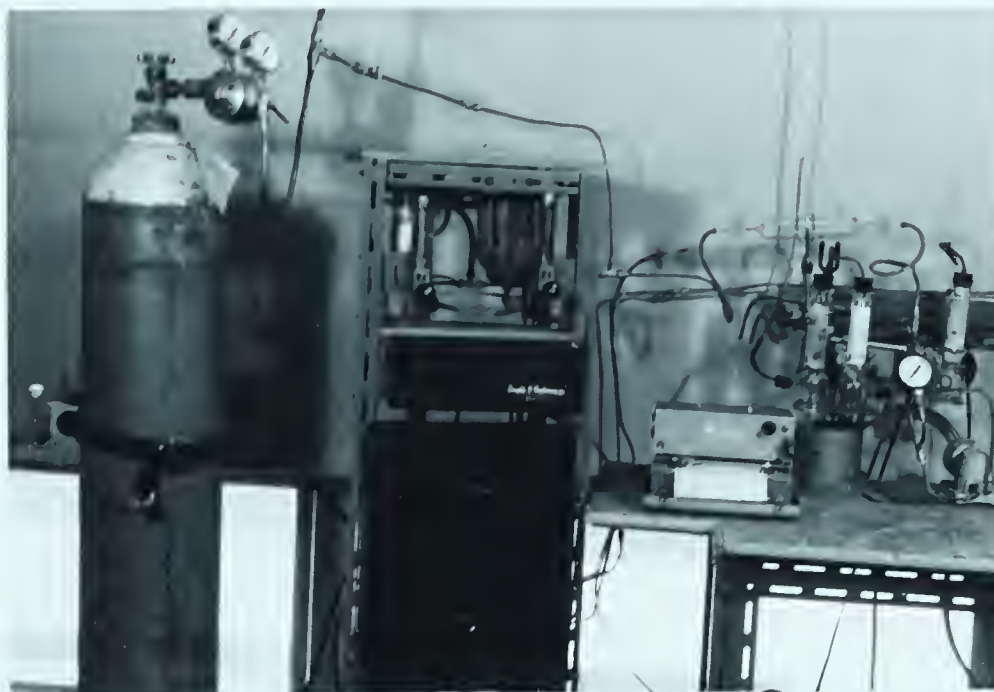


Fig. 21. The Beckman oxygen analyzer





## 8 THE CONTROL BOARD AND THE SAFETY DEVICE

A pyrotax temperature controller was used to control the temperature of the fuel gas in the iron casing of the burner. If the temperature in the iron casing was higher than the pre-set temperature (which was 600°F in this research). The solenoid valve for the gas supply was automatically shut off.

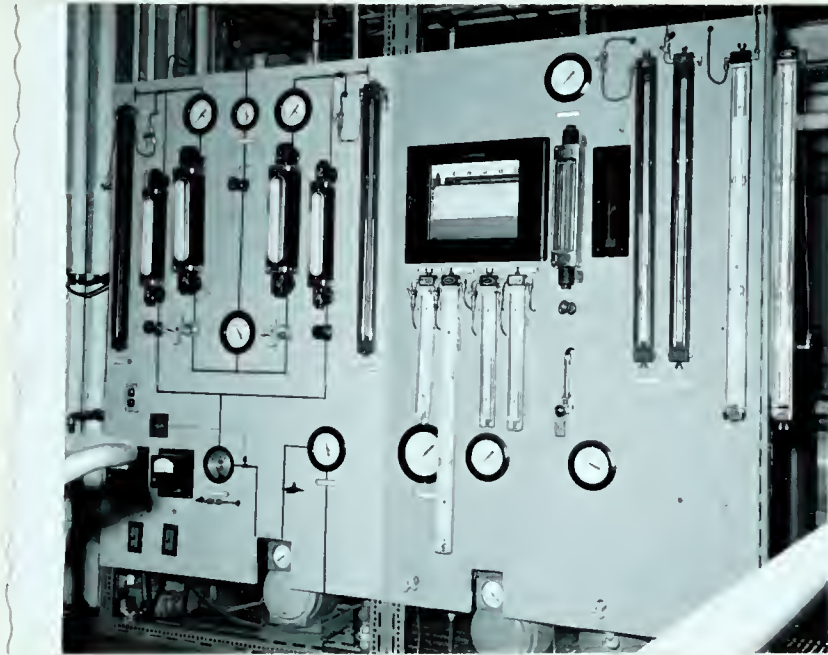


Fig. 22 The front view of the control board

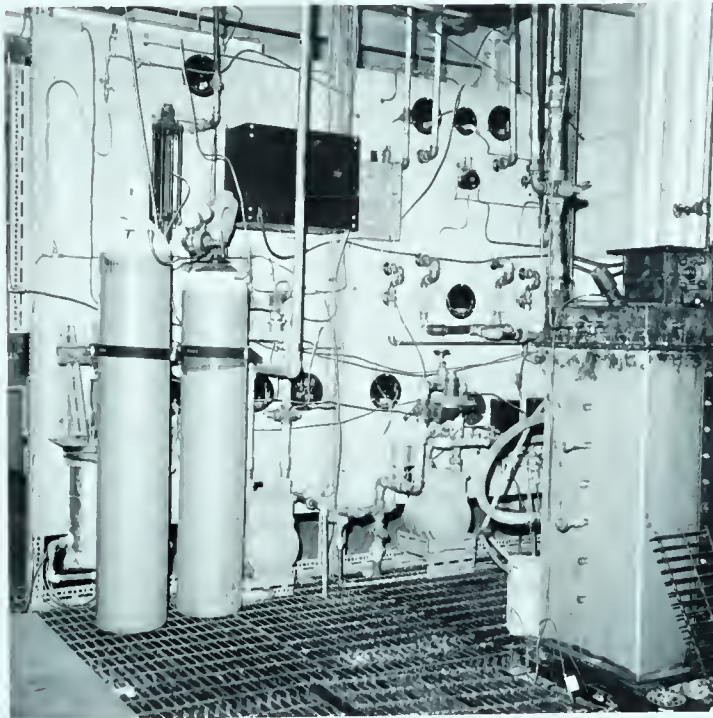


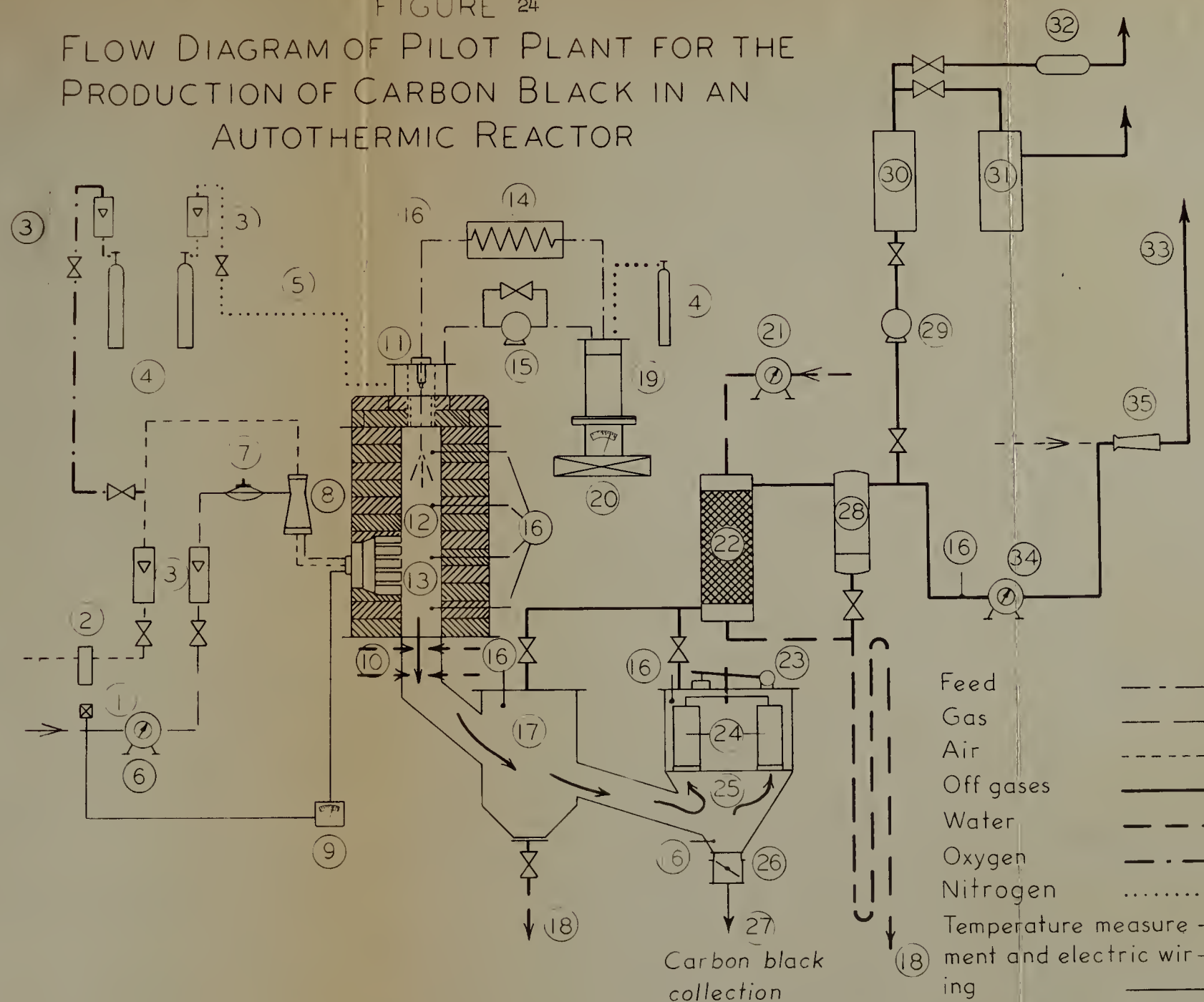
Fig. 23 The back view of the control board



# LEGEND

1. Nat. Gas Main Line and Solenoid Valve
2. Air filter
3. Flow rate meters
4. Oxygen and Nitrogen supply
5. Nitrogen dilution line
6. Natural gas meter
7. Zero gas governor
8. Air-Gas proportional mixer
9. Thermoelectric automatic shut down
10. Water spray quenching system
11. C.I. Bosch Diesel Injector feed assembly
12. Furnace autothermic reactor
13. Refractory Tunnel Combustor
14. Feed Preheater
15. Feed circulating pump
16. Thermocouple wells, and pressure tapping points
17. Water separator-collector
18. To waste and water drain
19. Feed storage vessel
20. Feed weighing scale
21. Water meter
22. Packed cooler
23. Slacking mechanism assembly
24. Glass cloth filter bags
25. Housing for carbon black collector
26. Swing gate valve
27. Carbon black collection
28. Water separator
29. Off-gas diaphragm pump
30. Off-gas Oxygen Analyzer
31. Specific gravity gas meter
32. Off-gas sampling bottle
33. Off-gas to the stack
34. Off-gas meter
35. Air ejector

FIGURE 24  
FLOW DIAGRAM OF PILOT PLANT FOR THE PRODUCTION OF CARBON BLACK IN AN AUTO THERMIC REACTOR







9. MISCELLANEOUS ITEMS OF EQUIPMENT

1. A trap for liquid water and a dryer for removing water vapour were connected in series in the air line before the air flowed into the rotameter.
2. One proportional mixer with a diaphragm control valve pre-mixed the air and the natural gas from the rotameters before they entered the iron casing of the burner.
3. There were three calibrated disc-type thermometers. Two measured separately the temperatures of the incoming air and natural gas before they entered the rotameters, and the third one measured the temperature of the finally cooled flue gases before they entered the gas meters.
4. A platform-type scale was used to measure the amount of diesel oil consumed.
5. Cylinders of compressed oxygen.
6. Electric Timer.
7. High pressure steam ejector for producing the required vacuum to draw the flue gas through the filtering bags, the packed cooler etc., and finally into the stack.



## VIII RESULTS

### 1. THE TABULATED OPERATING CONDITIONS OF THE TEST RUNS

In order to obtain a reasonably good conversion of the hydrocarbon feed into carbon black, the temperature of the reaction zone had to be maintained at about 2200<sup>o</sup> F. Consequently, all the other operating variables were all limited within narrow ranges which were as follows:

feed rate, diesel oil: 6-12 lb./hr.;      flowrate, natural gas:  
1.49-1.98 scfm

flowrate, air      : 13.01-20.55 scfm;      flowrate, oxygen:  
0.452-0.918 scfm

space velocity, reaction zone: 5.4-7.4 ft/sec.;      retention time: 0.14-0.19  
seconds.

Table 5 shows the operating conditions of each run.





TABLE 5. OPERATING CONDITIONS OF THE TEST RUNS

No. of run	FEED CHARACTERISTICS		
	material	injector	feed rate (lbs/hr.)
30	No. 1 diesel	modified GM injector	8.63 lbs/hr
31	"	"	11.60 lbs/hr
34	"	"	8.77 lbs/hr
35	"	"	9.73 lbs/hr
36	"	"	9.62 lbs/hr
37	"	"	6.0 lbs/hr
38	"	"	11.74 lbs/hr
39	"	"	12.08 lbs/hr
(B) 40	benzene	"Monarch" nozzle	21.92 lbs/hr



FURNACE CHARACTERISTICS

No.	fuel gases (SCFM) (760mm. 60°F)			Temperature, °F.		
	natural gas	dry air	O <sub>2</sub>	reaction zone	water spray	collecting bags
30	1.73	15.87	-	2165° 2250°	280°	210°
31	1.98	20.55	-	2005° 2150°	385° 430°	210° 255°
34	1.68	13.01	0.459	2150° 2250°	565° 692°	210°
35	1.66	13.43	0.458	2175° 2250°	607° 777°	251° 341°
36	1.68	13.21	0.452	2125° 2250°	585°	320°
37	1.49	13.37	-	2225° 2250°	540° 715°	250° 385°
38	1.68	16.19	-	2030° 2250°	607° 735°	251° 386°
39	1.91	17.57	0.906	2200° 2350°	650° 735°	225° 340°
40	1.97	14.75	0.918	2055° 2250°	605° 780°	250° 385°

The temperature of the reaction zone fluctuated within a narrow range, because the injection of the hydrocarbon feed had to be stopped during the shaking of the filtering bags.





FURNACE CHARACTERISTICS (continued)

No.	weight ratio of natural gas to feed (lb./lb.)	space velocity through reaction zone (ft./sec.)	retention time (sec.)
30	0.00845	6.3	0.16
31	0.0072	6.7	0.15
34	0.00808	5.7	0.18
35	0.0072	5.9	0.17
36	0.00737	5.8	0.17
37	0.01045	5.4	0.19
38	0.00603	6.7	0.15
39	0.00667	7.4	0.14



2. THE TABULATED CHEMICAL ANALYSIS OF THE CARBON

BLACK SAMPLE PRODUCED

For the determination of every property of the carbon black produced, two analyses of each carbon black sample were made. The results of the two analysis were very reasonably close to each other, and the average was made and tabulated.





TABLE 6. THE CHEMICAL ANALYSES OF THE CARBON BLACK SAMPLES

carbon black sample	yield (% dry basis)		weight loss through heating (%) at 105°C for 1 hr.	
	overall	carbon to carbon		
30	32.52	37.38	1.64 1.625	1.635
31	19.09	21.94	1.25 1.15	1.20
34	34.88	40.09	1.70 1.68	1.69
35	37.80	43.45	2.93 2.65	2.79
36	31.35	36.02	13.1 10.2	11.65
37	35.28	40.53	8.77 6.98	7.88
38	25.18	28.95	2.63 2.91	2.77
39	33.42	38.43	1.78 1.63	1.71
40 (benzene)	52.84	52.24	0.104	



PRODUCT CHARACTERISTICS

No.	(% dry basis)		pH (Blank = 6.4)	I <sub>2</sub> -number (ASTM) (dry basis)		benzene extract	
						%(dry basis)	time of extraction
30	0.285 0.260	0.273	6.35	75.15 76.07	75.61	8.15	3.0
31	0.302 0.288	0.295	6.55	128.46 126.87	127.67	19.00	8.0
34	0.108 0.094	0.101	7.65	73.56 72.99	73.28	6.58	2.5
35	0.183 0.154	0.169	7.05	68.06 67.18	67.62	4.42	2.5
36	0.534 0.578	0.556	5.65	89.82 93.54	91.68	12.56	4.0
37	0.127 0.120	0.124	6.85	63.47 61.60	62.54	3.18	2.5
38	0.099 0.133	0.116	6.85	94.14 92.60	93.37	15.42	4.5
39	0.079 0.069	0.074	7.35	80.83 81.47	81.15	10.20	4.0
40	0.147		6.95	38.10		2.50	1.5





No.	N <sub>2</sub> balance % deviation (based on calc. value)	carbon balance % deviation (based on calc. value)	H <sub>2</sub> balance % deviation (based on calc. value)
30	6.78%	5.66%	6.15%
31	2.52%	5.76%	6.23%
34	4.13%	4.81%	3.91%
35	4.0%	5.21%	4.05%
36	4.91%	4.95%	4.41%
37	3.55%	6.36%	4.06%
38	2.71%	7.10%	3.44%
39	2.99%	5.79%	6.78%

The typical analysis of natural gas, the flue gas analysis, and the sample calculation of the three kinds of material balance will be shown in the following pages.



1. Typical analysis of the natural gas (vol. %)

O<sub>2</sub>, 1.9%; N<sub>2</sub>, 8.4%; CO<sub>2</sub>, 0.1%; CH<sub>4</sub>, 73%; C<sub>2</sub>H<sub>6</sub>, 10.2%; C<sub>3</sub>H<sub>8</sub>, 3.9%  
(total 97.5%). Therefore, there was a basic deviation of 2.5% in the  
gas analysis.

2. The flue gas analysis (vol. %)

	Run 30	Run 31	Run 34	Run 35	Run 36	Run 37	Run 38	Run 39
H <sub>2</sub>	5.3	2.2	7.9	3.4	10.2	10.0	2.7	6.1
O <sub>2</sub>	1.1	1.0	1.1	1.6	1.7	1.4	1.1	1.5
N <sub>2</sub>	70.8	69.2	66.1	69.0	65.3	70.5	69.3	68.1
CO	14.3	19.1	13.4	21.8	10.4	0.5	20.8	10.5
CO <sub>2</sub>	6.3	4.6	8.5	1.1	9.4	16.1	0.7	10.6
CH <sub>4</sub>	2.2	3.3	2.7	3.1	2.4	1.5	4.8	3.2
C <sub>2</sub> H <sub>4</sub>	-	0.7	-	-	-	-	-	-
C <sub>2</sub> H <sub>2</sub>	-	-	0.3	-	0.6	-	0.6	-

3. Sample calculation of nitrogen balance of Run 30

atmospheric pressure = 712 mm Hg; temp. of flue gas = 21°C  
v.p., H<sub>2</sub>O, at 21°C = 18.65 mm Hg.

N <sub>2</sub> from dry air/min. = (15.87)(0.79)	=	12.53 scfm
N <sub>2</sub> from natural gas/min. = (1.73)(0.084)	, =	0.15 scfm
total		= 12.68 scfm

$$\text{N}_2\text{-out in flue gas} = \frac{(5 \times 60)}{28.4} + \frac{(5 \times 60)}{37.1} \frac{(712 - 18.65)(520)(0.708)}{(760)(530)}$$

$$= 11.82 \text{ scfm}$$

$$\text{difference} = 11.82 - 12.68 = -0.86 \text{ scfm}$$

$$\% \text{ deviation} = \frac{-0.86}{12.68} = -6.7\%$$





4. Sample calculation of carbon balance of Run 30

carbon to hydrogen ratio of No. 1 diesel = 6.65

$$\text{carbon from diesel feed} = \frac{(25.74)(6.65)}{(6.65+1)} = 22.368 \text{ lbs.}$$

actual time of the diesel injection = 179 minutes

$$\text{carbon from natural gas} = \frac{(1.73)(179)(12)}{(379)} = 9.81 \text{ lbs.}$$

total carbon from the diesel and the natural gas = 32.18 lbs.

Total vol. of flue gas at 712 mmHg and 21°C

$$= \frac{(179)(5)(60)}{(28.4)} + \frac{(179)(5)(60)}{(37.1)} = 3338 \text{ ft}^3$$

v.p. of water in flue gas at 21°C = 18.65 mmHg

the total percentage of CO, CO<sub>2</sub> and CH<sub>4</sub> = 22.8%

carbon in flue gas during injection

$$= \frac{(3338)(693.35) \times (0.228)(12)}{(760)(379)} = 21.99 \text{ lbs. carbon}$$

The wet carbon black produced in this run = 8.51 lbs.

The dry carbon black produced = (8.51) (0.9836) = 8.37 lbs.

total carbon - out = 30.36 lbs.

$$\% \text{ deviation} = \frac{30.36 - 32.18}{32.18} = -5.66\%$$

5. Sample calculation of hydrogen balance of Run 30

$$\text{hydrogen from the diesel feed} = \frac{(8.63)}{(60)(7.65)(2.016)} = 0.00952 \frac{\text{lb. mole}}{\text{min.}}$$

oxygen from the dry air/min = (15.87)(0.21) = 3.333 scfm; total mol. % of

hydrogen, including the hydrogen in methane = 5.3% + 2 x 2.2% = 9.7%

$$\text{hydrogen in the flue gas} = \frac{(11.82)(0.097)}{(0.708)(379)} = 0.004272 \frac{\text{lb. mole}}{\text{min.}}$$



$$\text{total mol. \% oxygen, including the oxygen in CO and CO}_2 = 1.1\% + \frac{14.3\%}{2} + 6.3\% = 14.55\%$$

$$\text{oxygen in the flue gas} = (16.695)(0.1455) = 2.429 \text{ scfm}$$

$$\text{The amount of oxygen converted into water} = \frac{(3.333 - 2.429)}{(379)}$$

$$= 0.002385 \frac{\text{lb. mole}}{\text{min.}}$$

$$\text{The amount of hydrogen converted into water} = 0.00477 \frac{\text{lb. mole}}{\text{min.}}$$

$$\begin{aligned} \text{The calculated amount of hydrogen in the flue gas} &= 0.00932 - 0.00477 \\ &= 0.00455 \frac{\text{lb. mole}}{\text{min.}} \end{aligned}$$

$$\% \text{ deviation in hydrogen} = \frac{0.004272 - 0.00455}{0.00455} = -6.15\%$$

Method used in the calculation of hydrogen balance:

- a. Under complete combustion condition, the hydrogen in the natural gas was all burned into water which was not shown in the flue gas analyses, because they were reported on dry basis. Therefore, any hydrogen (free or combined) in the flue gas must come from diesel oil.
- b. The difference between the amount of oxygen in the incoming air and that in the out-going flue gas was assumed to be due to the formation of water (also not shown in the flue gas analysis) with the hydrogen from the diesel oil. The moles of hydrogen converted into water was obviously twice the moles of oxygen consumed.
- c. Therefore, the amount of hydrogen from the in-coming diesel oil minus the amount of hydrogen converted into water should equal to the total amount of hydrogen in the flue gas.





### 3. THE RUBBER COMPOUNDING TESTS OF THE CARBON BLACK SAMPLES

According to the results of the rubber compounding tests of the carbon black samples produced from this research, the Goodrich Co., Canada, classified all of them as semi-reinforcing-furnace blacks. However, after comparing with those tests of the rubber compounded with the standard semi-reinforcing-furnace blacks (see Table 8A), one will realize that the rubber compounded with the carbon blacks produced from this research shows superior properties.





TABLE 7. RESULTS OF RUBBER COMPOUNDING TESTS

Stress Strain Compound T-214 Cured 25', 50', 65' at 292°F.

Sample No.	Cure -	Disper- sion	Durometer		Photometer		100%	200%	300%	400%	500%	600%	700%	Elongation
			Hardness Shore A	Uncured	Cured									
Sample No. 30														
95	25'		57	41	42		130	400	800	1420	2260	3200	3225 @	605%
	50'		65		41		250	600	1150	1830	2500	2810 @		515%
	65'		67		43		300	700	1280	1880	2550	2610 @		505%
Sample No. 31														
95	25'		58	44	35		200	470	900	1470	3190 @			595%
	50'		65		39		270	670	1140	1650	2300	2470 @		515%
	65'		65		41		280	680	1070	1580	2180	2325 @		515%
Sample No. 37														
95	25'		60	48	46		120	480	1100	1825	2700	3565 @		600%
	50'		66		44		250	820	1600	2470	3180	3300 @		515%
	65		67		43		300	880	1680	2680	3050 @			414%
Sample No. 39														
90	25'		58	52	38		200	480	860	1520	2460	3250	3290 @	610%
	50'		65		40		260	700	1300	1985	2860	3160 @		525%
	65'		65		44		300	800	1360	1955	2700 @			495%
Sample No. 40														
95	25'		56	50	52		200	520	1100	1850	2660	3160 @		575%
	50'		63		43		220	800	1580	2400	3170	3300 @		520%
	65'		65		46		360	1060	1800	2625	2920 @			435%

Notes: 1. All samples left no residue by Residue Test, U.S. No. 30.  
2. All samples showed staining by Test for staining.



## IX INTERPRETATION AND DISCUSSION OF RESULTS

The pressure in the furnace was maintained at practically atmospheric pressure. From this research it was found that the temperature of the reaction zone was the most important operating variable. There was no carbon black produced when the temperature of the reaction zone was below 2000°F. The run No. 31 gave the lowest yield ( 19% overall, and 22% carbon to carbon) while its temperature range (2005-2150°F) was also the lowest. From Fig. 25 , the optimum temperature of the reaction should be in the neighbourhood of 2200°F, at which the carbon-to-carbon yield would be 44%.

The loss in weight of the sample when heated at 105°C for one hour (the so-called heat loss) was mainly due to the loss of moisture upon heating. In order to avoid excessive moisture in the sample, the temperature around the collecting bag should be kept around 215°F.

The ash content of the carbon black produced was very low. This is a good indication that this process can produce very pure carbon black.

Generally speaking, the carbon blacks produced were practically neutral or slightly alkaline in character as shown from the pH values of the samples. However the No. 36 sample gave a slightly acidic pH (5.65).

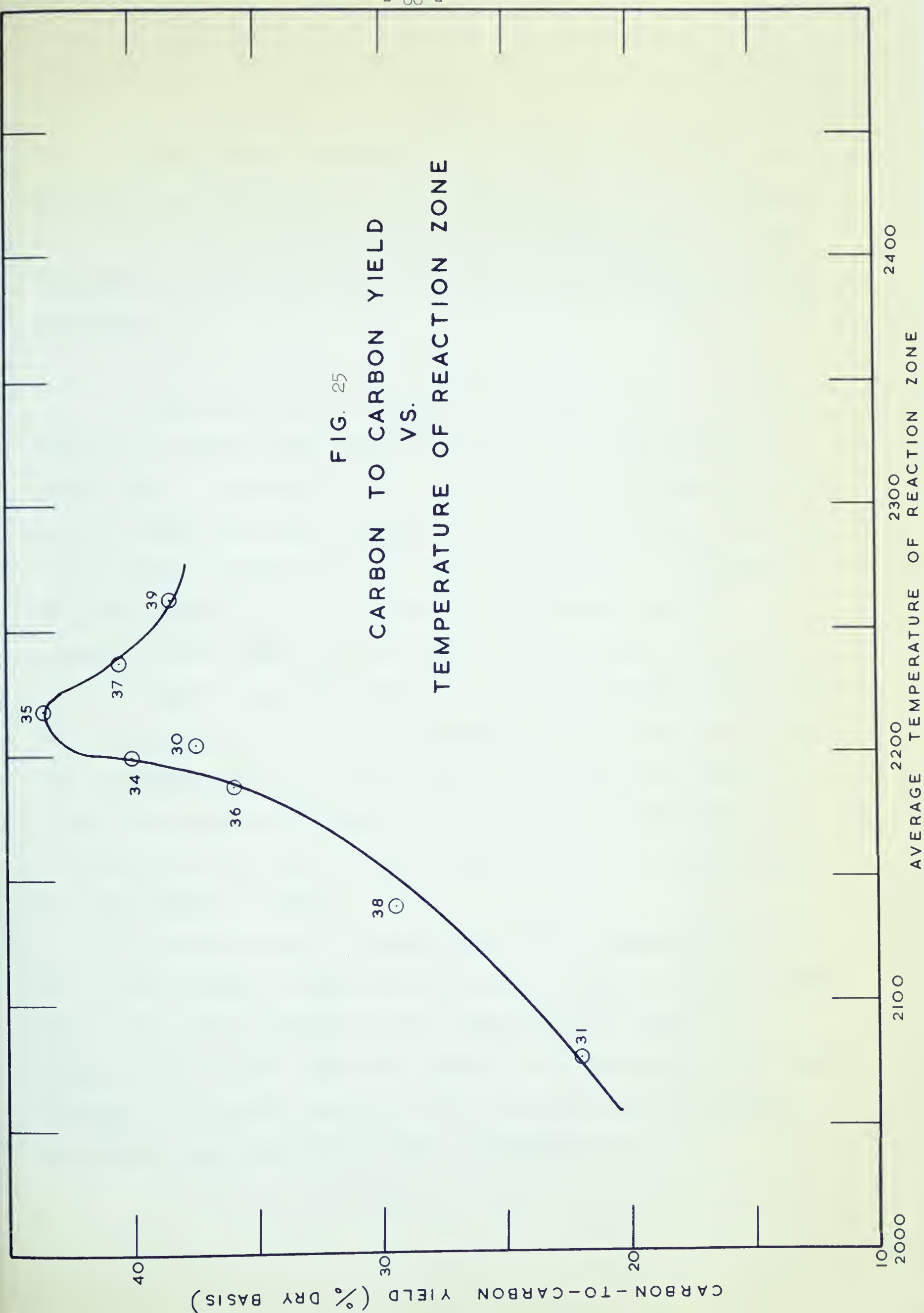
Three different ranges of feed rate were used, i.e., 6.0 lbs./hr. 8.63-9.73 lbs./hr., and 11.60-11.74 lbs./hr. Normally, the injections of diesel oil brought the temperature of the reaction zone below 2000°F under which no carbon black would be produced. Consequently the temperature in the reaction zone has to be raised to about 2200°F by either increasing the flowrate of natural gas or by adding oxygen.







FIG. 25  
CARBON TO CARBON YIELD  
VS.  
TEMPERATURE OF REACTION ZONE





Due to various restrictions, such as limited space in the research laboratory, physical properties of the collecting bags, etc., the quenching temperature of this research was limited to about 550°F. If the quenching temperature was much higher than 550°F, the glass-fibre filtering bags would be damaged.

High injection rate of diesel oil accompanied with low temperature range in the reaction zone (such as samples No. 31, 38 and 30) gave high iodine-number. The sample No. 37, which was produced at the lowest feed-rate and at the high side of the temperature range of the reaction zone, gave the lowest iodine-number when diesel oil was used as the feed. It was noticed that when benzene was used and injected into the reaction zone, the temperature in the zone went up, and that the iodine number was the lowest (38.1). Qualitatively, iodine number is directly proportional to the surface area (i.e. inversely proportional to the partical size) of the carbon black. When the temperature in the reaction zone was high, the carbon black was liable to be graphized into bigger graphite particles. Consequently the surface area per unit weight of carbon black became smaller and, therefore, the iodine number was smaller.

In this research, the iodine-numbers of the carbon black samples had a range from 127.67 (sample No. 31) to 38.1 (sample No. 40, from benzene). However, the rubber-compounding tests, conducted by B.F. Goodrich Co., Canada, grouped all the carbon black samples as SRF (semi-reinforcing furnace). Therefore, iodine-number seemed to be not a sensitive characteristic for classifying carbon blacks by the rubber compounding tests.





It has been claimed that the surface area per unit weight of carbon black could be estimated from the iodine-number by an empirical formula (61) which will appear in the Appendix.

The benzene-extract of the carbon black samples left a tar-like residue when the benzene was driven off through evaporation on the water-bath. High hydrocarbon feed rates and lower temperature range in the reaction zone resulted in high benzene-extract, i.e. higher iodine-number corresponded to higher benzene-extract, as shown in Fig. 26. The benzene extract of carbon black samples in this research ranged from a maximum 19% (sample No. 31 from diesel oil) through 3.18% (sample No. 37 from diesel oil) to a minimum 2.5% (from benzene). Since from rubber compounding tests, all these samples were classified as SRF carbon blacks, the benzene-extract was not a sensitive measure in differentiating carbon blacks.

Diesel oil was chosen as the principal raw material in this research. However, some additional information of producing carbon black from benzene by this process were also obtained from further experimental runs. Since benzene is aromatic, it was first expected that the carbon black produced should be in the class of oil-furnace-black. From the rubber compounding test, the carbon black produced from benzene by this process was still in the SRF class. This indicated that the aromatic hydrocarbon underwent similar reaction in this process as the aliphatic hydrocarbon.

In comparison with other commercial SRF carbon blacks, such as Kosmos 20 and Dixie 20, the carbon black samples produced by this process contained higher moisture contents (which can be cut down without much difficulty), but less ash content. Furthermore, the commercial SRF carbon blacks are generally basic in Character ( $\text{pH} = 9.9$ ).

The natural gas consumption for the production of carbon blacks in this research was as follows:





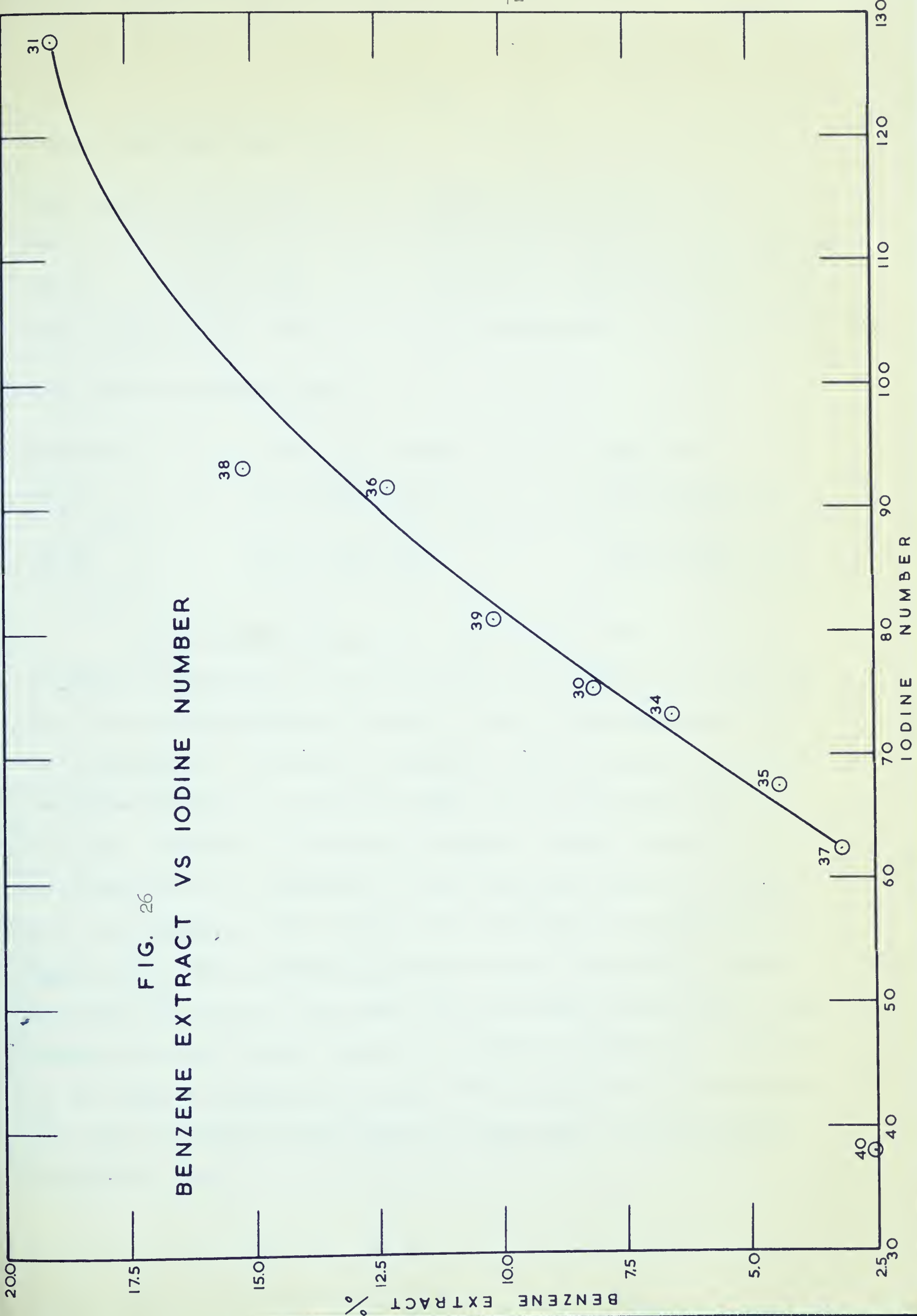


FIG. 26  
BENZENE EXTRACT VS IODINE NUMBER



When no additional oxygen was used

injection rate of diesel oil	natural gas consumed
run 37, 6.0 lbs./hr.	0.25 scfm/lb. oil, or 15 scf/hr./lb. oil
run 30, 8.63 lbs./hr.	0.2 scfm/lb. oil, or 12 scf/hr./lb. oil
runs 31, 38, 11.6-11.7 lbs./hr	0.17-0.145 scfm/lb. oil, or 10.2 scf/lb. oil

When additional oxygen was used

diesel rate	natural gas consumed	oxygen used
run 35, 9.73 lbs./hr	0.17 scfm/lb. oil or 10.8 scf/hr./lb. oil	0.049 scfm/lb. oil or 2.94 scf/hr./lb. oil
run 39, 12.0 lbs./hr.	0.16 scfm/lb. oil or 9.6 scf/hr./lb. oil	0.0755 scfm/lb. oil or 4.53 scf/hr./lb. oil

During the production of the carbon black in this research, the injection of hydrocarbon feed was intermittent, and the flow of the flue gas was by-passed and interrupted, in order to shake off the carbon black from the filtering bags. Therefore, no attempt was made for a heat balance, and the following calculated thermal efficiency can be considered as only a qualitative indication of the order of magnitude. In this calculation it was assumed the heat of combustion of the natural gas, which was considered to be pure methane, was used mainly to heat the products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) of the combustion, and the nitrogen (when air was used as a source of oxygen), and to heat and crack the diesel feed. It was assumed that there was no side-reaction which would consume the heat of combustion of natural gas. However, the low values of the calculated thermal efficiency may be a well indication that certain endothermic side-reactions did take place during the cracking of the diesel feed.





The calculated overall thermal efficiencies of runs 30, 31, 37 and 38 (with no addition of oxygen) ranged from 66.2% to 81.4%. The low values of the calculated thermal efficiency may be due to either high heat loss to the surrounding or certain endothermic side-reactions, or both. It is believed that better insulation will undoubtedly result in better thermal heat efficiency.



TABLE 8. CALCULATED THERMAL EFFICIENCY

No. of run	Fuel gases (scfm. 760 mm. 60F)			feed rate (lb./hr.)	Overall yield (% dry basis)	Approx. ave.temp. reaction zone (°F)	Calc. thermal efficiency (%)
	nat. gas	dry air	O <sub>2</sub>				
30	1.73	15.87	--	8.63	32.52	2200	65.8
31	1.98	20.55	--	11.60	19.09	2100	81.4
34	1.68	13.01	0.459	8.77	34.88	2200	62.3
35	1.66	13.43	0.458	9.73	37.80	2200	65.5
36	1.68	13.21	0.452	9.62	31.35	2200	63.9
37	1.49	13.37	--	6.0	35.28	2200	55.9
38	1.68	16.19	--	11.74	25.18	2100	67.7
39	1.91	17.57	0.906	12.08	33.42	2260	84.7

The estimation of heat required for cracking No. 1 diesel oil and the sample calculation of overall thermal efficiency will be shown on the following pages.





Estimation of Heat Required for Cracking No. 1 Diesel Oil.

Since No. 1 diesel oil had been chosen as the feed, the next step was to estimate the amount of heat required for cracking the diesel oil. Nevertheless the carbon and hydrogen content, or the carbon to hydrogen ratio, of the diesel oil had to be first determined. At the time of the investigation no such information was available. Therefore, it had to be calculated from Linden and Othmer's nomograph and empirical equations (59).

1) From API Gravity, aniline point ( $^{\circ}\text{F}$ ) and 50% ASTM boiling point ( $^{\circ}\text{F}$ ) of diesel oil, the weight ratio ( $R'$ ) of carbon to hydrogen, of pure hydrocarbon compounds with equivalent physical properties, was found from the given nomograph which claims an arithmetic average deviation of 1.1% and a maximum deviation of  $(-2.6)$  to  $(+2.4)\%$ . For the No. 1 diesel oil used in this research, the value of  $R'$  was found to be 6.23.

2) Calculation of weight ratio ( $R$ ) of carbon to hydrogen, for No. 1 to No. 5 fuel oils and a variety of related fractions, from the following simplified equation:

$$R = R' + 0.0417 \left[ (R')^2 - 30.0 \right]$$

which claims an an arithmetic average deviation of 1.2% and a maximum deviation of  $(-3.2)$  to  $(+2.6)\%$ . For the No. 1 diesel oil used in this research.

$$R = 6.23 + 0.0417 \left[ (6.23)^2 - 30.0 \right] = 6.601$$



3) The heat of formation ( $Q_f$ , B.T.U./lb.) of the No. 1 diesel oil used at 77°F and constant pressure, was calculated from the following equation:

$$Q_f = 1995 - 199R = 1995 - 199 (6.601) = 680 \text{ B.T.U./lb.}$$

Calculation of Heat Required to Decompose One Pound of No. 1 Diesel Oil to Carbon and Hydrogen, if the Cracking Temperature is Assumed to be 2200°F

Basis: 1 lb. diesel oil feed at 77°F

enthalpy of carbon at 2200°F = 9,800 B.T.U./lb-mole;

enthalpy of carbon at 77°F = 0

enthalpy of hydrogen at 2200°F = 15,100 B.T.U./lb-mole;

enthalpy of hydrogen at 77°F = 0

heat of formation of diesel oil = 680 B.T.U./lb

Sensible heat required to heat carbon in diesel oil to 2200°F =

$$\frac{6.6}{7.6} \left( \frac{9,800.0}{12} \right) = 710 \text{ B.T.U./lb}$$

Sensible heat required to heat hydrogen in diesel oil to 2200°F =

$$\frac{1.0}{7.6} \frac{15,100.0}{2016} = 988 \text{ B.T.U./lb.}$$

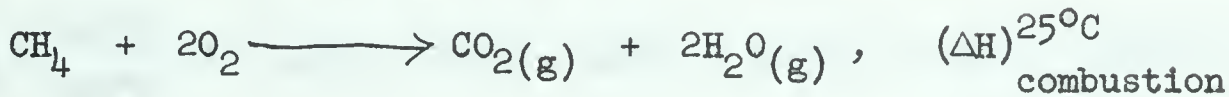
∴ total heat required for cracking diesel oil = 2378 B.T.U./lb





# Sample Calculation of Overall Thermal Efficiency

1. For Run -30 (burning with air):



4.38 lbs/hr.    17.5 lbs/hr.    12.05 lbs/hr.    9.85 lbs/hr.

= 21,500 B.T.U./lb

94,200 B.T.U./hr.

$$(C_p)_{\text{CO}_2} = 6.85 + (8.53 \times 10^{-3}) (T) - (24.75 \times 10^{-7}) (T^2)$$

$$25^\circ\text{C} = 298^\circ\text{K}; \quad 2200^\circ\text{F} = 1478^\circ\text{K}$$

$$\therefore (\Delta H_{\text{CO}_2})_{298^\circ\text{K}}^{1478^\circ\text{K}} = H_0 + (6.85) (1180) + (4.26 \times 10^{-3}) (2,096 \times 10^3) - (8.25 \times 10^{-7}) (320.4 \times 10^7)$$

since,  $H_0$  (the integration constant for  $\text{CO}_2$ ) = -2,173 c.h.u./lb.-mole

$$\begin{aligned} \therefore (\Delta H_{\text{CO}_2})_{298^\circ\text{K}}^{1478^\circ\text{K}} &= -2,173 + 8,080 + 8,930 - 2,660 \\ &= 17,010 - 4,833 = 12,177 \text{ c.h.u./lb.mole} \\ &= 499 \text{ B.T.U./lb.} \end{aligned}$$

$$(C_p)_{\text{H}_2\text{O}} = 6.89 + (3.283 \times 10^{-3}) (T) + (3.43 \times 10^{-7}) (T^2)$$

$$H_0 = -2,007 \text{ c.h.u./lb.mole}$$

$$\begin{aligned} \therefore (\Delta H_{\text{H}_2\text{O}})_{298^\circ\text{K}}^{1478^\circ\text{K}} &= -2,007 + (6.89) (1180) + (1.642 \times 10^{-3}) (2,096 \times 10^3) + \\ &\quad (1.14 \times 10^{-7}) (320.4 \times 10^7) \\ &= -2,007 + 8,130 + 3,440 + 365 = 11,935 - 2,007 \\ &= 9,928 \text{ c.h.u./lb. mole} = 993 \text{ B.T.U./lb.} \end{aligned}$$



$$(C_p)_{N_2} = 6.30 + (1.819 \times 10^{-3}) (T) - (3.45 \times 10^{-7}) (T^2)$$

$$H_o = -1,787 \text{ c.h.u./lb. mole}$$

$$\begin{aligned} (\Delta H_{N_2})_{298^\circ K}^{1478^\circ K} &= -1,787 + (6.3) (1180) + (0.909 \times 10^{-3}) (2,096 \times 10^3) - \\ &\quad (1.15 \times 10^{-7}) (320.4 \times 10^7) \\ &= -1,787 + 7430 + 1905 - 368 = 9335 - 2155 \\ &= 7180 \text{ c.h.u./lb. mole} = 462 \text{ B.T.U./lb.} \end{aligned}$$

Heat required to crack the diesel feed,

$$= (2378) (8.63) = 20,500 \text{ B.T.U./hr}$$

Heat required to heat  $N_2$  from the air,

$$\frac{(15.87)(60)(0.79)(28)(462)}{(379)} = 25,600 \text{ B.T.U./hr}$$

Heat required to heat  $CO_2 = (12.05) (499)$

$$= 6,020 \text{ B.T.U./hr.}$$

Heat required to heat water vapour,

$$= (9.85) (993) = 9,780 \text{ B.T.U./hr.}$$

---


$$\text{Total} = 61,900 \text{ B.T.U./hr.}$$

$$\therefore \text{ thermal efficiency} = \frac{\text{heat consumed}}{\text{heat generated}}$$

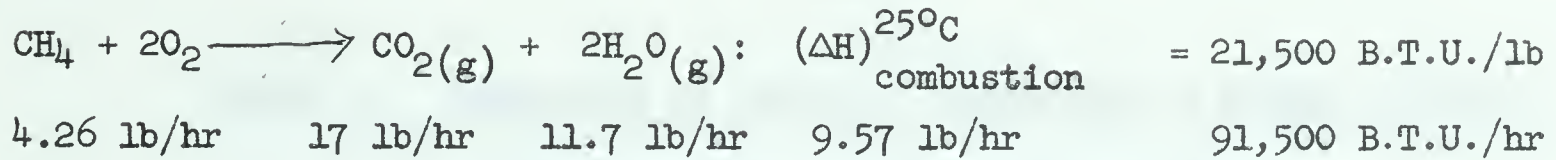
$$= \frac{61,900}{94,200} = 65.8\%$$

2. For run -34 (with the addition of oxygen):

Approximate weight of hydrocarbon (in terms of methane)

$$\text{in natural gas used} = \frac{(1.68) (60) (16)}{(379)} = 4.26 \text{ lbs./hr.}$$





Heat required for heating diesel feed,

$$= (2378) (8.77) = 20,800 \text{ B.T.U./hr.}$$

Heat required for heating  $\text{N}_2$  from air,

$$= \frac{(13.01) (25,600)}{(15.87)} = 20,950 \text{ B.T.U./hr.}$$

$$\text{Heat required for heating CO}_2 = (11.7) (499) = 5,830 \text{ B.T.U./hr.}$$

Heat required for heating water vapour,

$$= (9.57) (993) = 9,500 \text{ B.T.U./hr.}$$

---

$$\text{Total} = 57,080 \text{ B.T.U./hr.}$$

$$\therefore \text{thermal efficiency} = \frac{57,080}{91,500} = 62.3\%$$





TABLE 8A. COMPARISON OF PHYSICAL PROPERTIES OF RUBBER PRODUCTS  
COMPOUNDED WITH VARIOUS CARBON BLACKS

Comparison of some of the physical properties of rubber product when compounded with the commercial SRF carbon black (Kosmos/Dixie, 20) with those when compounded with the carbon blacks produced by this process:

properties of compounded rubber (synthetic)	time of cure 293°F (minute)	SRF Kosmos/ Dixie 20	carbon black produced by this process				
			No. 30	No. 31	No. 37	No. 39	No. 40 (benzene)
modulus at 300% elongation, psi	25	1000	800	900	1100	860	1100
	50	1050	1150	1140	1600	1300	1580
	65	1100	1280	1070	1680	1360	1800
tensile strength (psi)	25	1900	3225	3190	3565	3290	3160
	50	2000	2810	2470	3300	3160	3300
	65	2000	2610	2325	3050	2700	2920
% elongation at break	25	650	700	595	600	700	600
	50	525	600	600	600	600	600
	65	500	600	600	500	500	500
shore hardness	25	52	57	58	60	58	56
	50	54	65	65	66	65	63
	65	55	67	65	67	65	65

It is obvious that the rubber products exhibited superior properties when they were compounded with the carbon blacks produced by this process to those when compounded with the commercial SRF carbon black.



## X CONCLUSION

By this autothermic process, a commercial grade carbon black was produced. It was classified by the rubber compounding tests conducted by B.F. Goodrich (Canada) Ltd., to be semi-reinforcing-furnace black although some of its physical properties (such as ash content etc.) and some of the properties of the compounded rubber (such as modulus at 300% elongation, tensile strength, % elongation at break, shore hardness, etc.) were superior to those when the rubber was compounded with the commercial grade SFR from the present market. Moreover, the equipment appeared to be simpler than those in commercial usage for the manufacture of furnace black. Therefore it is recommended that more research work should be continued in order to fully develop this new process for the manufacture of carbon black from even cheaper liquid hydrocarbons and for the manufacture of other types of carbon blacks such as HAF (high-abrasive-furnace), SAF (super-abrasive-furnace), etc.





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A P P E N D I X    A





## GENERAL PROCEDURES OF THE OPERATION

The general procedures of the operation were as follows:

1. Set the oxygen analyzer and its recorder to work. Lighted the burner and heated up the reaction chamber to the desired temperature. This used to take about 2 to 3 hours. A sample of the fluegas and the steady operating conditions, before the introduction of diesel oil were taken and recorded.
2. Took the reading of the initial total weight of the jar and the diesel oil.
3. Set the throttle of the atomizer to give the approximate desired feed rate of diesel oil, and lubricated all the moving parts and joints of the injection system. Closed the outlet valve on the top of the small collecting tank, and open the outlet valve of the big collecting tank.
4. Started the diesel injection and the electric timer. Also marked the starting time on the recording chart of the temperature recorder. Several steps followed immediately.
  - a. the temperature of the reaction chamber dropped sharply.
  - b. either increasing the flowrate of the reactor gas or adding oxygen gas, or both, to bring the temperature of the reaction chamber back to the desired range.
  - c. adjusted the flow rate of cooling water to the sprayers in order to get the desired quenching temperature.
  - d. adjusted the flow rate of either compressed air or high pressure steam to the ejector in order to maintain the pressure in the reaction chamber at atmospheric pressure.



5. Adjusted the flow rate of cooling water to the packed cooler to ensure a complete cooling of the flue gases.
6. Started the knocking mechanism to shake the bags when the pressure drop across the bags was going up steadily, as it was shown from the manometer.
7. When the pressure drop across the filtering bags was between 10-15 inches of water (generally taking about 25 minutes), the diesel oil injection was shut-off. Several steps followed immediately.
  - a. Marked the interruption of the diesel oil injection on the recording chart of the temperature recorder.
  - b. Cut down the flow rate of compressed air or high pressure steam to the ejector in order to keep atmospheric pressure in the reaction chamber.
  - c. Opened the outlet valve on the top of the small collecting tank and closed the outlet valve on the top of the big collecting tank so that the flue gas free from the carbon black might by-pass the filtering bags and flow directly to the packed cooler. Opened the valve at the conical bottom of the small collecting tank to drain out the excessive quenching water.
  - d. Started and continued the knocking and shaking of the filtering bags for 5 to 8 minutes.
  - e. Opened the swing gate valve and collected the carbon black into the polyethylene bag.
  - f. Closed the swing gate valve, opened the outlet valve of the big collecting tank, and closed the outlet valve of the small collecting tank.





8. Started the diesel oil injection again, and marked the time of starting of diesel oil injection on the recording chart of the temperature recorder. Repeated the operating cycle until about 8 pounds of carbon had been produced.



A P P E N D I X    B



The abbreviations of current types of carbon black, their manufacturing process and basic fuel used. (10, bibliography)

<u>Type</u>	<u>Description</u>	<u>Manufacturing Process</u>	<u>Basic Fuel</u>
EPC	Easy processing channel	Channel	gas
MPC	Medium processing channel, highest in tensile strength	"	"
HPC	Hard processing channel	"	"
CC	Conductive channel	"	"
STC	Surface treated channel	"	"
SAF	Super abrasion furnace, highest reinforcement, but relatively the most difficult to process	Furnace	oil
ISAF	Intermediate super abrasion furnace, more usual and less expensive	"	"
HAF	High abrasion furnace	"	"
FEF (MAF)	Fast extrusion furnace (medium abrasion furnace), best for extrusion	"	gas
FF	Fine furnace, lowest in compression set	"	oil - gas
GPF	General purpose furnace	"	gas
SRF	Semi-reinforcing furnace, highest in resiliency	"	"
CF	Conductive furnace	"	"
SCF	Super conductive furnace, highest in conductivity	"	"
HMF	High Modulus furnace	"	"
FT	Fine thermal	"	"
MT	Medium thermal, lowest in durometer, relatively the easiest to process and lowest reinforcement	"	"





A P P E N D I X   C



GENERAL TERMINOLOGIES RELATED TO RUBBER COMPOUNDING TEST

1. Designations of Rubber Family:

A. ASTM Designation: D1418 - 58 T

- a. BR - butadiene rubbers
- b. IR - isoprene rubbers, synthetic
- c. CR - chloroprene rubbers
- d. NR - natural rubbers, (isoprene rubber, natural)
- e. ABR - acrylate - butadiene rubbers
- f. IIR - isobutylene - isoprene rubbers
- g. NBR - nitrile - butadiene rubbers
- h. NCR - nitrile - chloroprene rubbers
- i. PBR - pyridine - butadiene rubbers
- j. SBR - Styrene-butadiene rubbers (formerly referred to as GR-S)
- k. SCR - styrene - chloroprene rubbers
- l. SIR - styrene - isoprene rubbers

B. Some conventional industrial symbols: (13, bibliography)

- 1. GR-S 1500 - cold rubber
- 2. GR-S 1000 - hot rubber
- 3. GR-S 1712 - (formerly known as X - 730) - oil masterbatch polymer
- 4. Natural rubber
- 5. Butyl (GR-1-18) - copolymer of isobutylene (97.5%) and isoprene (2.5%)
- 6. Butyl reclaim (UI-7715) "





2. Terms Relating to Rubber and Rubber - Like Materials: (ASTM Designation: 1566-58T)

a. Abrasion Resistance Index - A measure of the abrasion resistance of a vulcanized material or synthetic rubber compound relative to that of a standard rubber compound under specified conditions and expressed as:

$$\text{Abrasion Index} = \frac{S}{T} \times 100$$

where:

S = volume of a standard rubber compound, and

T = volume loss of the rubber being evaluated.

b. Grain - The uni-directional orientation of rubber or filler particles resulting in anisotropy of a rubber compound.

c. Hardness - The resistance to indentation.

d. International Rubber Hardness Degree - a measure of hardness, the magnitude of which is derived from the depth of penetration of a specified indenter into a specimen under specified conditions. The scale is so chosen the 0-degree would represent a material showing no measurable resistance to indentation, and 100-degree would represent a material showing no measurable indentation (see ASTM Designation: D1415)

e. Mechanical stability of Latex - Resistance to clotting of latex when subjected to mechanical shear under specified conditions.

f. Swelling - The increase in volume or linear dimensions of a specimen immersed in a liquid or exposed to a vapour.

g. Tear Strength - The maximum load required to tear apart a specified specimen, the load acting substantially parallel to the major axis of the test specimen.

h. Tensile strength - the maximum tensile stress applied during stretching a specimen, to rupture.



i. Tensile Stress - The applied force per unit of original cross-section area of a specimen.

j. Tensile stress at Given Elongation - The tensile stress required to stretch a uniform section of a specimen to a given elongation.

k. Specimen - A piece of material appropriately shaped and prepared so that it is ready to use for a test.

3. Standard loadings of various types of carbon black for testing in natural and synthetic rubber: (ASTM Designation: D 1522 - 58T)



TABLE 9. LOADING OF CARBON BLACKS IN RUBBER

Types of Carbon Black	Loading in natural rubber (parts by wt. per 100 parts rubber hydrocarbon)	Loading in styrene-butadiene rubber (parts by wt. per 100 parts rubber hydrocarbons)
Chanel blacks	40	40
SAF	40	40
ISAF	40	40
HAF	40	40
FF	40	40
FEF	50	50
CF	40	40
HMF	50	50
GPF	50	50
SRF	50	50
FT	75	75
MT	75	75





A P P E N D I X    D



PHYSICAL AND CHEMICAL PROPERTIES OF CARBON BLACK AND  
THE ASTM NUMBER OF THEIR TESTING METHODS (7, 8 Bibliography)

1. Average Particle Diameter (millimicrons):

The particle diameters are determined with electron microscope and the measurements are averaged statistically. Expressions of particle diameter calculated from the nitrogen surface area or obtained by other methods and techniques may give substantially different values.

In general, tensile strength of elastomers and the area under the stress-strain curve tend to increase as the particle size of carbon black incorporated decreases. The stiffness (modulus) of the cured stock also increases but much less markedly, while resilience, resistance to heat generation on flexing and plasticity decrease.

In paint and ink, colour intensity and oil absorption increase with decreasing particle size, but tinting strength reaches a maximum in the 25 m u range and then levels off. Absorption of most materials increases with decreasing particle size as a result of the increased area.

2. Nigrometer Index:

Diffuse reflectance from a specially prepared sample of carbon black and linseed-oil varnish is measured by comparison with the intensity of the light cast on a translucent screen produced by a movable lamp attached to a scale previously calibrated. A standard tile having a nigrometer value of 95 is used.





3. Tinting Strength (SFR = 100):

Relative tinting strength of carbon blacks in a paste with zinc oxide and an oil vehicle is measured according to the Analytical Text Procedure established by the ASTM-D24 Committee of Carbon Black Industry.

4. Oil Absorption:

Oil absorption is the number of cubic centimeters of standard linseed oil which is added to one gram of carbon black to form a firm coherent round mass of the mixture. It is a relative measure of the structure and oil demand, and generally, a good indication of the relative viscosity of many ink and paint systems.

5. Iodine Adsorption:

Iodine adsorption number is the number of milligrams of iodine adsorbed per gram of carbon black. The analytical test follows the procedure of ASTM Designation: D 1510 - 57T

6. PH Value:

The PH value of carbon black is determined by the standard test method of ASTM Designation: D 1512 - 57T

7. Surface Area:

a) By Nitrogen adsorption method -

The surface area of each black is determined from its low temperature nitrogen adsorption isotherm according to the procedure of



Brunauer, Emmett, and Teller. (25) By this procedure, the volume ( $V_m$ ) of nitrogen required for a complete monolayer at  $-196^{\circ}\text{C}$  is obtained. In computing the surface,  $(16.24^{\circ}\text{A})^2$  was employed as the cross sectional area of the nitrogen molecule.

b) By Dannenberg equation

$$\text{Calculated surface area (M}^2\text{/gram)} = \frac{(91) (A-B)}{(A \times C)} - \frac{4.5}{C}$$

A = cc of 0.01 N of  $\text{Na}_2\text{S}_2\text{O}_3$  used in blank

B = cc of 0.01 N of  $\text{Na}_2\text{S}_2\text{O}_3$  used in test run

C = grams sample used in test run.

8. Volatile content of carbon black: ASTM Designation: D 1620 - 58T:

This method covers a procedure for determining the volatile material other than moisture in the carbon black by heating in electric furnace at  $950 \pm 20^{\circ}\text{C}$  for approximately half-an-hour.

9. Benzene Extract used in this research:

a) One gram of dry carbon black was put into an alundum extraction thimble which is put into the throat of a soxhlet extractor.

b) 50 cc of C.P. benzene was added into the extraction flask which was then heated on a hot plate for 3 - 4 hours until the extracting liquid from the thimble was practically colorless.

c) The extracting liquid was transferred into a weighed beaker, and was evaporated to dryness on a water-bath.

d) The residue and the beaker was then weighed.





10. Ash Content:

The analytical test follows the procedure of ASTM Designation:

D 1506 - 57 T

- a) Ignite the crucible with cover in the muffle furnace at  $550 \pm 25^{\circ}\text{C}$  for 1 hour.
- b) Dry an adequate sample of carbon black for 1 hour at  $105^{\circ}\text{C}$
- c) 2 gm. of dry sample in the crucible is heated at  $550^{\circ}\text{C}$  for 1 hour in the muffle furnace, with the cover removed.

11. Heat Loss of Carbon Black - ASTM Designation: D 1509 - 57 T

This method covers a procedure for determining the heating loss of carbon black at  $105^{\circ}\text{C}$ . This heating loss consists primarily of moisture, but traces of other volatile materials may also be lost. The method is not applicable to treated carbon blacks which contain added volatile materials.

12. Sulfur Content of Carbon Black - ASTM Designation: D 1619 - 58 T

The following two methods are included:

- a) Oxygen Bomb Calorimeter: determined as  $\text{BaSO}_4$
- b) Combustion Furnace: titrating with standard  $\text{KIO}_3$  - KI solution

13. Sieve Residue from Carbon Black - ASTM Designation: D 1514 - 57 T

This method covers a procedure for determining the water wash sieve residue in regular untreated carbon blacks. It may not be applicable to oil-treated carbon blacks because the oil would prevent proper wetting of the black by the water.





14. Tap Density:

By determining the density of carbon black after it has been tapped by a specially designed machine for exactly 30 minutes.

15. Pour Density - ASTM Designation D 1513 - 57 T

16. Particle Shape:

Carbon black particles are generally spherical and are tightly cohered or fused into chains or agglomerates which are sufficiently stable through-out many of the commercial applications. The stiffness of a dispersion in rubber is greatly increased by such agglomerates.

17. Surface Nature:

Carbon atoms, carbon-oxygen chemisorbed complexes  $(C_2O_3)_n$  and  $(CO)_n$  and  $H_2$  are the chief constituents of the surface of carbon blacks. The  $(C_2O_3)_n$  complexes have the tendency to retard the rate of cure in rubber. All types of carbon-oxygen complexes have the tendency to reduce modulus of the compounded rubber, to reduce oil absorption, and to favor longer flow in ink blacks.

18. Crystal Structure:

The increase in crystallite size produced by heating for long periods at temperatures of  $800^{\circ}C$  or higher is accompanied by a decrease in stiffening power in rubber.

19. Attrition of Pelleted Carbon Black - ASTM Designation: D 1507 - 57 T

This method covers a procedure for the determination of the mechanical stability of pelleted carbon black.



20. Fines Content of Pelleted Carbon Black - ASTM Designation: D 1508 - 57 T

This method covers a procedure for determining the fines content of pelleted carbon black.

21. Pellet size Distribution of Carbon Black - ASTM Designation D 1511 - 57 T

22. Discoloration of Benzene by Carbon Black - ASTM Designation D 1618 - 58 T

This method covers a procedure for determining the degree of discoloration of benzene by carbon black, by means of photoelectric colorimeter or spectrophotometer.





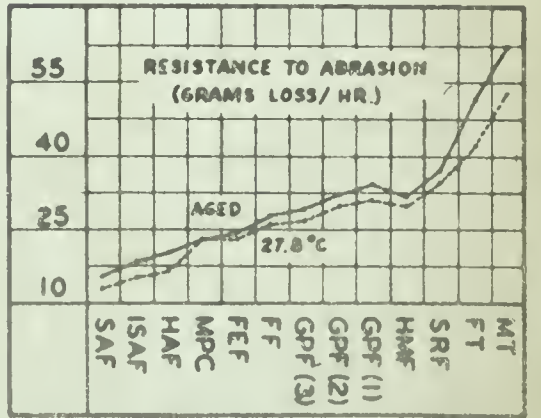
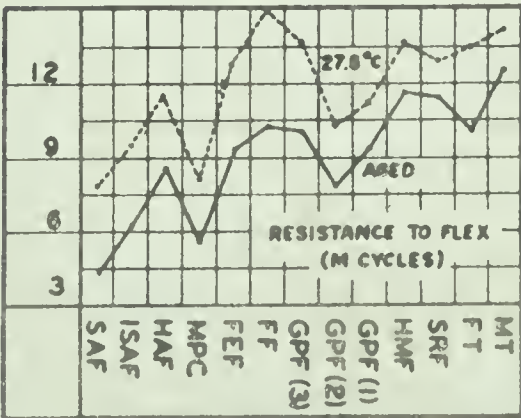
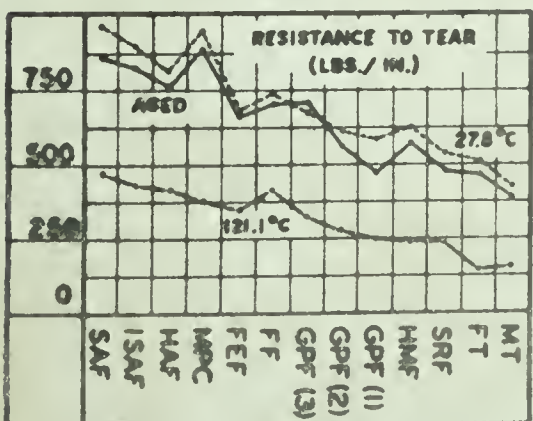
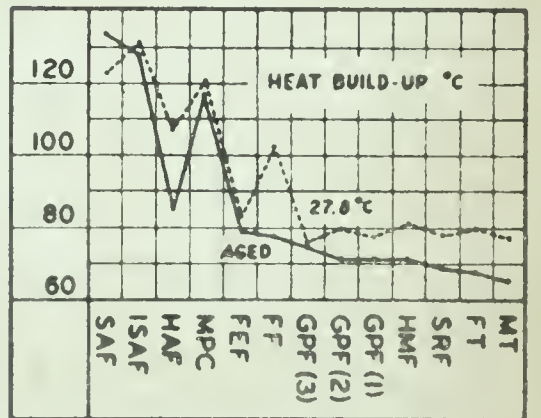
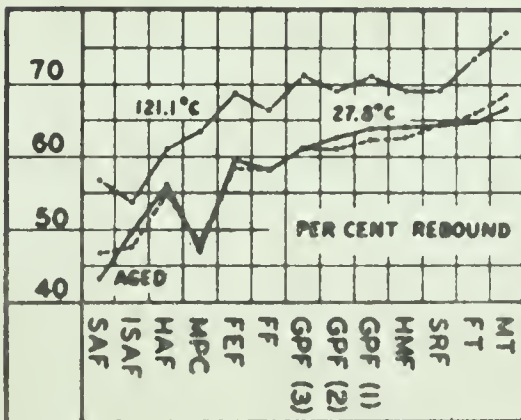
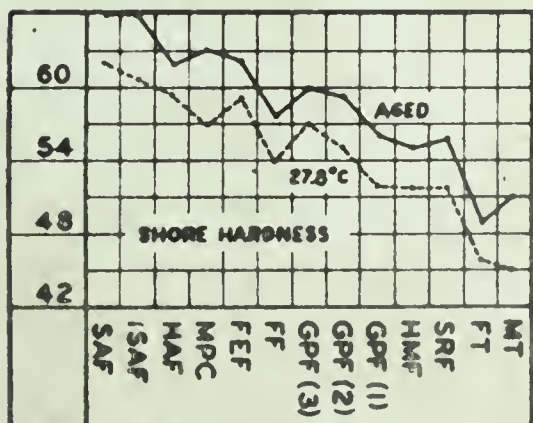
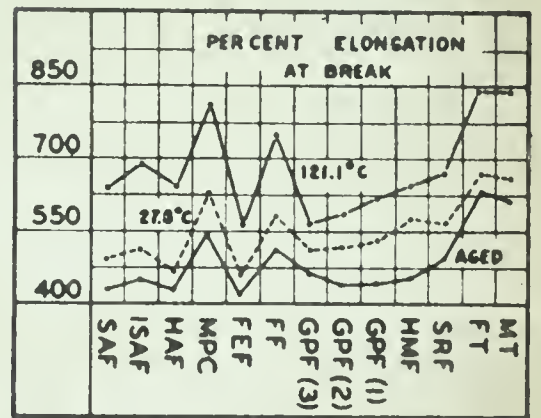
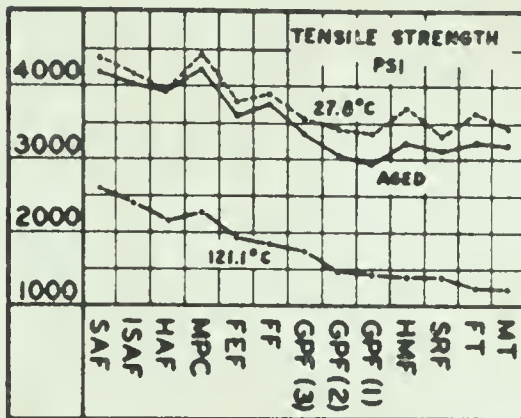
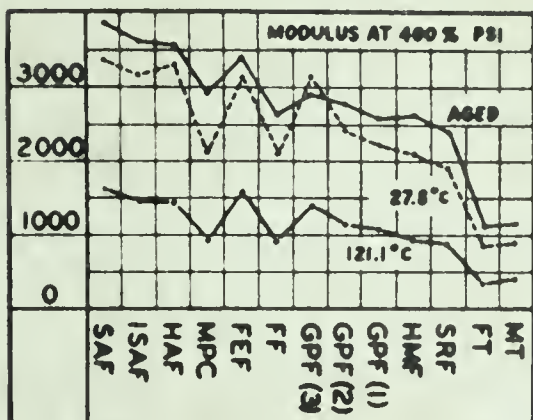
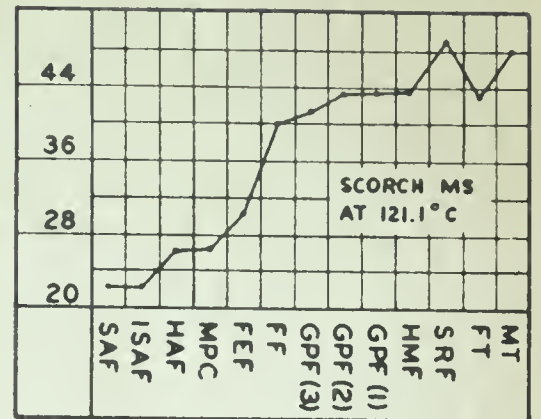
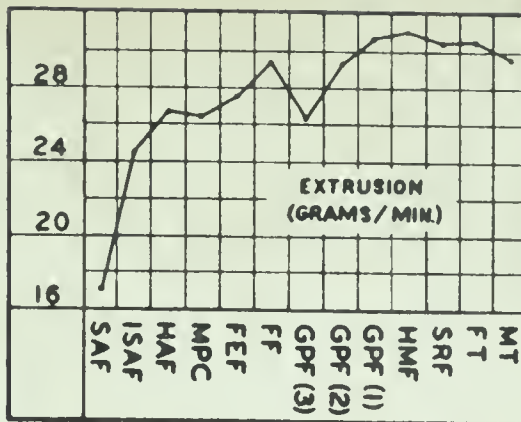
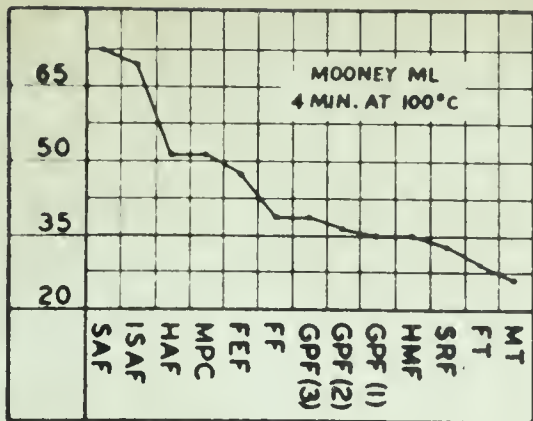
APPENDIX-E

**table 10, TRENDS IN PHYSICAL AND CHEMICAL PROPERTIES OF VARIOUS TYPES OF CARBON BLACK (10, Bibliography)**

Type	Carbon black	Sur- face area, sq. m./ gm.	Par- ticle Dia- meter, m $\mu$	Mois- ture, % <sub>o</sub>	Ash, % <sub>o</sub>	Vola- tile mat- ter, % <sub>o</sub>	Benzol ex- tract, % <sub>o</sub>	pH	Nigro- meter index	Tint com- par- ison	Oil absorp- tion, c.c./100 gm. black	Iodine ad- sorp- tion, % <sub>o</sub>	Specific gravity	Ap- parent den- sity, lb./ cu. ft.
MPC	Kosmobile S-66/ Dixie- densed S-66	120.4	26.0	1.36	0.06	5.77	0.03	4.9	85.7	373	116	17.4	1.80	24.0
CC	Voltex/ Dixie Voltex	387.0	8.1	1.30	0.05	5.05	0.01	4.9	70.0	398	160	25.6	1.80	18.5
SAF	Kosmos 85/ Dixie 85	127.2	24.6	1.97	0.27	1.92	0.17	9.6	86.1	400	152	16.3	1.80	19.1
ISAF	Kosmos 70/ Dixie 70	101.8	30.7	1.45	0.78	1.45	0.11	9.1	90.0	385	143	13.2	1.80	22.6
HAF	Kosmos 60/ Dixie 60	69.2	45.2	0.71	0.24	1.63	0.05	9.2	93.9	366	126	9.8	1.80	25.6
FEF	Kosmos 50/ Dixie 50	39.0	80.0	0.46	0.11	0.91	0.09	9.3	99.9	308	139	5.1	1.80	23.6
FF	Statex B	76.1	41.0	0.63	0.47	1.23	0.01	9.2	94.6	355	86	7.1	1.80	29.0
GPF	Kosmos 35/ Dixie 35	31.8	98.3	0.07	0.16	0.58	0.08	9.9	101.1	285	117	3.9	1.80	21.2
GPF	Kosmos 45/ Dixie 45	26.2	119.3	0.29	0.47	0.63	0.12	8.9	100.8	256	86	2.1	1.80	25.0
HMF	Kosmos 40/ Dixie 40	33.0	95.0	0.15	0.54	0.65	0.13	10.1	101.8	287	81	3.9	1.80	31.2
SRF	Kosmos 20/ Dixie 20	19.5	160.0	0.11	0.61	0.74	0.13	9.9	104.1	240	85	3.0	1.80	32.0
SCF	Vulcan SC	249.3	12.5	0.40	0.55	1.54	0.23	8.5	90.7	388	145	30.9	1.80	22.7
FT	P-33	14.0	223.7	0.11	0.08	0.67	1.33	9.5	108.9	216	51	3.4	1.80	24.0
MT	Thermax	6.6	472.8	0.07	1.49	0.96	0.17	7.4	116.2	100	39	1.0	1.80	29.0



fig. 27 (10, Bibliography)





A P P E N D I X - F

TABULATED COMPARISON OF VARIOUS CARBON BLACK COMPOUNDED WITH RUBBER





TABLE 11 — PHYSICAL TESTS ON UNCURED AND CURED RUBBER

I. VARIOUS RUBBERS AND BLACKS (11, Bibliography)

A. NATURAL RUBBER<sup>1</sup>

Type Carbon Black	ISAF Kosmos/ Dixie 70 31	HAF Kosmos/ Dixie 60 45	EPC Kosmobile/ Dixiedensed 77 26	FEF Kosmos/ Dixie 50 80	GPF Kosmos/ Dixie 35 98	SRF Kosmos/ Dixie 20 160	MT Thermax
Particle Size (Mu.)	31	45	26	80	98	160	473
<b>Processing</b>							
Banbury							
Maximum Stock Temperature (°F) .....	224	230	218	238	235	226	206
Total Power (Watt-Hours) .....	2130	2150	1970	2170	2100	1965	1780
Plasticity							
Mooney Viscosity (ML, 4' at 212°F) .....	67	58	46	52	35	29	24
Williams, h <sub>1</sub> (MM) .....	2.90	2.28	2.21	1.80	1.47	1.35	1.12
Dillon (Seconds) .....	5.1	3.4	2.1	2.5	1.3	1.0	0.9
Extrusion							
Grams/Minute .....	22.2	26.0	31.0	28.2	36.5	34.4	33.3
Meters/Minute .....	6.9	7.4	8.3	8.0	9.9	8.8	7.6
Grams/Meter .....	3.23	3.53	3.73	3.51	3.68	3.92	4.40
Shrinkage and Swell							
Mill Shrinkage (%) .....	24	26	38	21	20	28	57
Extruder Shrinkage (%) .....	62.1	65.3	66.9	65.1	66.4	68.5	72.0
Extruder Swell (%) .....	152	171	179	171	176	190	220
Dillon Swell (%) .....	70	70	95	67	73	86	136
Williams Recovery, h <sub>2</sub> (MM) .....	3.18	2.62	2.54	2.24	1.86	1.58	1.42
Scorch, MS at 250°F (Minutes) .....	18	17	26	21	24	36	53
<b>Reinforcement</b>							
	Cure, Min. 280°F.						
Modulus at 400% .....	30	2660	2540	1810	2360	2210	1380
Elongation (psi) .....		3060	2860	2140	2660	2450	1670
	60	3240	2980	2260	2780	2560	1800
	75	3300	3120	2330	2860	2610	1900
Tensile Strength (psi) .....	30	4000	3800	4240	3360	3380	2900
	45	4300	4000	4240	3580	3460	3250
	60	4380	4000	4240	3580	3460	3250
	75	4200	3880	4170	3500	3460	3250
% Elongation at Break .....	30	555	565	655	525	555	625
	45	530	525	610	520	530	625
	60	525	520	600	510	520	600
	75	490	490	590	480	515	595
Shore Hardness .....	30	60	58	60	56	55	49
	45	63	61	63	59	58	53
	60	64	62	65	60	59	55
	75	65	63	65	61	60	56
% Rebound .....	30	45	49	47	54	58	59
	45	45	50	47	56	61	62
	60	45	50	47	57	59	60
De Mattia Cut Growth .....	60	6,362	7,692	5,813	8,982	9,980	9,187
(Flexes to Failure)							10,970
Heat Build-Up (°F) .....	60	188	170	177	159	159	165
% Compression .....		11.8	7.6	9.3	4.7	5.9	6.8
% Set .....		11.6	5.2	6.8	3.6	4.4	5.6
Angle Abrasion (Gms. Loss/Hr.) .....	60	12.6	13.7	21.1	19.8	23.0	32.0
							50.9

<sup>1</sup>Formulation: Natural Rubber, 100; EPC Black, 50; Zinc Oxide, 3; Flexamine, 1.3; Stearic Acid, 2; Paraflux, 3; Santocure, 0.6; Retarder W, 1; Sulfur, 2.4.  
Natural Rubber, 100; Furnace Black, 50; Zinc Oxide, 3; Flexamine, 1.3; Stearic Acid, 2; Paraflux, 3; Santocure, 0.35; Retarder W, 1; Sulfur, 2.25.



TABLE 12— PHYSICAL TESTS ON UNCURED AND CURED RUBBER (Continued)

I. VARIOUS RUBBERS AND BLACKS (Continued) (11, Bibliography)

B. COLD SYNTHETIC RUBBER (1500)<sup>1</sup>

Type		ISAF	HAF	EPC	FEF	GPF	SRF	MT
Carbon Black		Kosmos/ Dixie 70 31	Kosmos/ Dixie 60 45	Kosmobile/ Dixiedensed 77 26	Kosmos/ Dixie 50 80	Kosmos/ Dixie 35 98	Kosmos/ Dixie 20 160	Thermax 473
Article	Size (Mu.)							
Processing								
Banbury								
Maximum Stock Temperature (°F) .....		238	232	254	247	256	236	220
Total Power (Watt-Hours) .....		2390	2190	2450	2265	2380	2295	2220
Plasticity								
Mooney Viscosity (ML, 4' at 212°F) .....		74	68	69	68	59	51	44
Williams, h <sub>1</sub> (MM) .....		3.02	2.95	2.67	2.73	2.06	1.80	1.57
Dillon (Seconds) .....		3.1	2.5	3.8	2.0	2.1	2.1	1.6
Extrusion								
Grams/Minute .....		36.2	36.3	28.2	34.9	37.6	33.6	28.3
Meters/Minute .....		13.4	12.6	8.4	13.3	13.1	9.7	6.1
Grams/Meter .....		2.71	2.88	3.35	2.63	2.87	3.45	4.66
Shrinkage and Swell								
Mill Shrinkage (%) .....		20	26	35	22	25	37	58
Extruder Shrinkage (%) .....		54.1	56.8	62.9	52.7	56.6	64.0	73.3
Extruder Swell (%) .....		101	113	159	92	110	155	243
Dillon Swell (%) .....		51	54	76	45	57	79	—
Williams Recovery, h <sub>2</sub> (MM) .....		3.71	3.43	3.22	3.05	2.54	2.21	1.88
Scorch, MS at 250°F (Minutes) .....		21	17	37	21	26	36	40
Reinforcement		Cure, Min. 293°F.						
Modulus at 300% .....		25	2150	2010	1240	1810	1400	790
Elongation (psi) .....		40	2600	2440	1820	2140	1700	1000
		60	2980	2630	2140	2300	1820	1100
		90	3060	2740	2220	2330	1840	1120
Tensile Strength (psi) .....		25	3750	3570	3720	2720	2460	1900
		40	3900	3800	3320	3020	2480	2000
		60	3780	3910	2930	2940	2550	2000
		90	3750	4080	2630	2940	2480	1880
% Elongation at Break .....		25	460	460	590	485	490	650
		40	405	425	450	460	430	555
		60	360	420	370	380	420	505
		90	355	415	340	375	380	460
Shore Hardness .....		25	61	59	60	58	57	52
		40	63	60	63	60	59	54
		60	64	61	65	61	60	55
		90	65	61	65	62	60	56
% Rebound .....		40	42	46	46	52	56	57
		60	42	46	46	52	56	57
		90	42	46	46	52	56	57
De Mattia Cut Growth .....		90	6,350	16,313	2,149	6,367	3,993	8,537
(Flexes to Failure)								7,897
Heat Build-Up (°F) .....		90	195	191	175	186	176	175
% Compression .....			1.1	0.6	0.6	0.6	0.6	2.3
% Set .....			2.8	2.4	0.8	1.6	1.2	1.6
Angle Abrasion (Gms. Loss/Hr.) .....		90	8.2	10.7	18.4	21.4	29.4	43.8
								103.1

Formulation: GR-S 1500, 100; EPC Black, 50; Zinc Oxide, 5; Stearic Acid, 1.5; Paraflux, 5; MBT, 1.2; DPG, 0.4; Sulfur, 2.5.  
GR-S 1500, 100; Furnace Black, 50; Zinc Oxide, 5; Stearic Acid, 1.5; Paraflux, 5; MBT, 0.8; DPG, 0.25; Sulfur, 2.





**table 13,** EVALUATION OF VARIOUS TYPES OF CARBON BLACK IN NATURAL RUBBER AT INCREASED LOADINGS (10, Bibliography)

Type		SAF	ISAF	HAF	MPC	FEF	FF	GPF	GPF	HMF	SRF	FT	MT
Carbon black		Kosmos 85 Dixie 85	Kosmos 70 Dixie 70	Kosmos 60 Dixie 60	Kosmobile S-66 Dixiedensed S-66	Kosmos 50 Dixie 50	Statex B	Kosmos 35 Dixie 35	Kosmos 45 Dixie 45	Kosmos 40 Dixie 40	Kosmos 20 Dixie 20	P-33	Thermax
	Loading (parts/ 100 RHC)												
Maximum stock tem- perature (° C.)	20	113.9	116.1	116.1	103.9	112.8	113.4	117.2	112.8	115.0	116.1	108.9	108.9
	30	111.1	106.7	107.8	101.1	118.3	104.5	107.2	112.2	101.6	104.5	100.0	100.0
	40	116.1	110.0	109.4	98.3	121.1	101.6	107.2	104.5	102.2	104.5	100.0	98.9
	50	114.5	115.0	117.8	98.9	117.8	103.9	111.1	103.9	101.1	97.8	98.9	95.6
	60	127.2	119.4	120.0	101.1	123.9	105.6	115.5	100.5	101.6	103.4	93.9	92.2
	70	—	—	—	—	—	104.5	117.8	111.1	107.8	106.7	93.4	92.2
	80	—	—	—	—	—	112.2	118.3	112.8	108.9	108.9	90.0	89.4
	90	—	—	—	—	—	—	—	—	110.0	110.5	91.6	89.4
	100	—	—	—	—	—	—	—	—	—	—	90.0	88.9
	110	—	—	—	—	—	—	—	—	—	—	90.0	88.9
	120	—	—	—	—	—	—	—	—	—	—	—	87.8
Total power (watt- hours)	20	2150	2050	2040	2020	2070	2025	2030	2055	2040	2040	1960	1850
	30	2100	2060	2050	1925	2020	1930	1970	1880	1940	1960	1845	1850
	40	2110	2010	2015	1860	1990	1840	1900	1795	1835	1853	1795	1690
	50	2275	2230	2235	1970	2210	2015	2090	1875	1840	1840	1705	1690
	60	2215	2050	2050	1840	2030	1790	1915	1770	1740	1760	1570	1580
	70	—	—	—	—	—	1840	2020	1870	1760	1780	1550	1530
	80	—	—	—	—	—	1800	1915	1820	1750	1740	1500	1445
	90	—	—	—	—	—	—	—	—	1765	1755	1460	1420
	100	—	—	—	—	—	—	—	—	—	—	1500	1440
	110	—	—	—	—	—	—	—	—	—	—	1445	1400
	120	—	—	—	—	—	—	—	—	—	—	—	1390
Mooney viscosity (ML-4' at 100° C.)	20	31	24	24	28	26	24	25	27	25	24	23	25
	30	38	36	34	32	30	28	29	26	29	28	27	26
	40	48	43	41	40	34	32	33	30	32	30	25	26
	50	72	69	51	51	48	38	38	35	35	33	28	26
	60	81	73	61	58	52	40	43	39	38	38	29	30
	70	—	—	—	—	—	51	52	43	43	42	33	31



**table 13—continued** (10, Bibliography)

Type		SAF	ISAF	HAF	MPC	FEF	FF	GPF	GPF	HMF	SRF	FT	MT
Carbon black		Kosmos 85 Dixie 85	Kosmos 70 Dixie 70	Kosmos 60 Dixie 60	Kosmobile S-66 Dixiedensed S-66	Kosmos 50 Dixie 50	Statex B	Kosmos 35 Dixie 35	Kosmos 45 Dixie 45	Kosmos 40 Dixie 40	Kosmos 20 Dixie 20	P-33	Thermax
	Loading (parts/ 100 RHC)												
% Elongation at break*	20	670	655	650	720	645	675	650	640	660	670	725	710
	30	655	635	605	720	575	660	610	620	635	640	725	710
	40	600	600	565	700	530	655	590	585	610	610	720	655
	50	505	520	470	645	465	580	510	545	580	570	675	655
	60	450	470	455	620	440	595	500	535	575	595	660	665
	70	—	—	—	—	—	545	415	460	505	530	660	625
	80	—	—	—	—	—	490	405	410	460	470	635	610
	90	—	—	—	—	—	—	—	—	420	425	620	600
	100	—	—	—	—	—	—	—	—	—	—	580	580
	110	—	—	—	—	—	—	—	—	—	—	595	590
	120	—	—	—	—	—	—	—	—	—	—	—	540
Shore hardness*	20	45	45	43	44	45	42	44	42	42	42	40	40
	30	50	50	49	48	49	45	47	46	45	45	42	41
	40	55	55	53	52	53	49	50	49	48	48	44	42
	50	62	61	59	56	59	54	57	52	52	52	46	45
	60	67	66	63	61	63	57	60	56	55	55	49	45
	70	—	—	—	—	—	60	64	60	59	58	51	47
	80	—	—	—	—	—	65	67	64	62	61	53	48
	90	—	—	—	—	—	—	—	—	66	65	56	51
	100	—	—	—	—	—	—	—	—	—	—	58	52
	110	—	—	—	—	—	—	—	—	—	—	60	54
	120	—	—	—	—	—	—	—	—	—	—	—	56
% Rebound at 26.7° C.*	20	68	70	71	70	72	72	73	73	73	73	74	76
	30	57	60	65	57	69	65	69	70	69	70	72	72
	40	51	53	60	51	63	58	63	65	63	66	67	70
	50	49	49	57	51	60	60	62	64	63	66	67	70
	60	39	43	50	41	55	49	62	61	59	62	63	69
	70	—	—	—	—	—	43	54	56	55	57	60	64
	80	—	—	—	—	—	41	47	52	53	52	56	65
	90	—	—	—	—	—	—	—	—	49	52	52	61
	100	—	—	—	—	—	—	—	—	—	—	55	62
	110	—	—	—	—	—	—	—	—	—	—	55	61
	120	—	—	—	—	—	—	—	—	—	—	—	60

**Formulation.** Channel: Natural rubber, 100; zinc oxide, 3; stearic acid, 2; Santoflex 35, 1; Paraflux, 6; Sulphur, 2.50; Santocure, 0.6; carbon black, 50. Banbury mix.

Furnace: Natural rubber, 100; zinc oxide, 3; stearic acid, 2; Santoflex 35, 1; Paraflux, 6; sulphur, 2.25; Santocure, 0.5; Vultrol, 1; carbon black, 50. Banbury mix.

\* 40 minute cure at 137.8° C.





Table 13—continued	(10, Bibliography)
Table 13—continued	(10, Bibliography)

Type		SAF	ISAF	HAF	MPC	FEF	FF	GPF	GPF	HMF	SRF	FT	MT
		Kosmos 85 Dixie 85	Kosmos 70 Dixie 70	Kosmos 60 Dixie 60	Kosmobile S-66 Dixiedensed S-66	Kosmos 50 Dixie 50	Statex B	Kosmos 35 Dixie 35	Kosmos 45 Dixie 45	Kosmos 40 Dixie 40	Kosmos 20 Dixie 20	P-33	Thermax
	Loading (parts/ 100 RHC)												
Mooney viscosity (continued)	80	—	—	—	—	—	55	57	49	46	44	32	30
	90	—	—	—	—	—	—	—	—	53	50	34	31
	100	—	—	—	—	—	—	—	—	—	—	37	34
	110	—	—	—	—	—	—	—	—	—	—	40	36
	120	—	—	—	—	—	—	—	—	—	—	—	36
Mill shrinkage (%)	20	56	55	54	56	55	62	53	61	61	61	62	68
	30	46	43	47	51	43	55	48	51	56	56	58	60
	40	35	34	35	44	27	46	37	40	47	44	56	58
	50	28	26	23	40	21	36	26	34	37	37	63	54
	60	14	16	18	29	14	34	19	27	30	29	51	48
	70	—	—	—	—	—	24	14	19	22	22	41	45
	80	—	—	—	—	—	19	12	14	18	17	35	40
	90	—	—	—	—	—	—	—	—	13	13	33	36
	100	—	—	—	—	—	—	—	—	—	—	29	35
	110	—	—	—	—	—	—	—	—	—	—	24	32
	120	—	—	—	—	—	—	—	—	—	—	—	29
Modulus at 400% elongation (p.s.i.)*	20	1400	1370	1350	1000	1380	950	1230	1050	1000	950	600	600
	30	1960	1860	1880	1230	2030	1320	1750	1480	1360	1300	700	750
	40	2580	2520	2520	1600	2560	1600	2000	1820	1800	1700	780	850
	50	3350	3260	3400	2040	3240	2060	2730	2240	2100	1970	920	1000
	60	3710	3500	3460	2250	3300	2200	2830	2370	2240	2100	930	1020
	70	—	—	—	—	—	2550	3220	2800	2590	2370	1130	1320
	80	—	—	—	—	—	3000	3330	2940	2800	2540	1250	1400
	90	—	—	—	—	—	—	—	—	2980	2680	1360	1560
	100	—	—	—	—	—	—	—	—	—	—	1520	1620
	110	—	—	—	—	—	—	—	—	—	—	1480	1680
	120	—	—	—	—	—	—	—	—	—	—	—	1640
Tensile strength (p.s.i.)*	20	4500	4260	4150	4630	4050	4020	3980	3840	3850	3950	3620	3660
	30	4770	4570	4220	4840	3800	4460	4050	3780	4060	3980	4080	3860
	40	4670	4680	4250	4860	3910	4370	4000	3780	3950	3820	4010	3620
	50	4380	4270	4070	4540	3800	3850	3670	3480	3720	3410	3900	3600
	60	4230	4150	4020	4370	3620	3900	3560	3370	3620	3400	3580	3520
	70	—	—	—	—	—	3580	3350	3190	3340	3140	3460	3300
	80	—	—	—	—	—	3560	3370	3000	3200	2930	3180	3050
	90	—	—	—	—	—	—	—	—	3100	2780	2990	2780
	100	—	—	—	—	—	—	—	—	—	—	2500	2610
	110	—	—	—	—	—	—	—	—	—	—	2560	2530
	120	—	—	—	—	—	—	—	—	—	—	—	2350





TABLE-14 COMPARISON OF VARIOUS TYPES OF CARBON BLACKS IN  
BUTADINE-STYRENE (GR-S) SYNTHETIC RUBBER WITH 50 LOADING (12. Biblio.)

Types	Mooney Viscosity	Mooney Scorch	Shrinkage (%)	Extrusion (gm/min)	Modulus (lbs/in)
SAF	82	23	17	36.1	2600
ISAF	74	21	20	36.2	2980
HAF	64	26	26	36.4	2280
MPC	69	37	35	28.2	2140
FEF	67	25	19	39.1	2240
FF	52	32	37	31.6	1270
HMF	51	35	37	32.7	1190
GPF	58	25	26	37.7	1580
SRF	51	36	37	33.6	1100
MT	44	40	58	28.3	460

Types	Hardness	Abrasion (gm. loss/hr.)	Particle Diameter (mμ)	Tensile Strength (lbs./in)
SAF	66	7.9	25	4180
ISAF	64	8.2	31	3780
HAF	61	12.1	45	3380
MPC	65	18.4	26	2930
FEF	62	22.9	80	2980
FF	56	25.5	41	2760
HMF	55	35.9	95	2220
GPF	59	34.6	98	2280
SRF	55	43.8	160	2000
MT	49	103.1	473	1140



TABLE-15 EFFECT OF INCREASED LOADING OF 4-MAIN TYPES OF  
CARBON BLACKS IN SYNTHETIC RUBBER (12, Biblio.)

Loading	Tensile Strength				Shore Hardness			
	HAF	MPC	SRF	MT	HAF	MPC	SRF	MT
20	4150	4630	3950	3360	43	44	42	40
30	4220	4840	3980	3860	49	48	45	41
40	4250	4860	3820	3620	53	52	48	42
50	4070	4540	3410	3600	59	56	52	45
60	4020	4370	3400	3520	63	61	55	45
70			3140	3300			58	47
80			2930	3050			61	48
90			2780	2780			65	51
100				2610				52
110				2530				54
120				2350				56





TABLE-16    TEAR RESISTANCE OF VARIOUS  
TYPES OF CARBON BLACK IN NATURAL RUBBER (11, Biblio.)

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<u>Type Black</u>	<u>Tear Resistance at Room Temperature (lbs./in. thickness)</u>
SAF	964
ISAF	906
HAF	822
FEF	669
FF	718
GPF	651
HMF	625
SRF	544
FT	509
MT	425



TABLE-17 RESISTANCE TO ABRASION OF RUBBERS COMPOUNDED  
WITH VARIOUS TYPES OF BLACK (gm. loss/hr.) (11, Biblio.)

Type Black	Particle Diameter, $\mu$	Natural Rubber
SAF	25	12.4
ISAF	31	14.4
HAF	45	16.2
EFC	26	21.1
FEF	80	21.9
FF	41	26.2
GPE	98	26.6
HMF	95	29.8
SRF	160	34.0
FT	224	42.7
MT	473	52.8
Hot Synthetic Rubber (1000)	Cold Synthetic Rubber (1500)	Oil-Extended Rubber (1712)
7.4	7.9	6.6
9.2	8.2	7.4
10.5	10.7	8.8
14.1	18.4	16.2
19.0	21.4	16.2
18.2	25.5	19.2
22.2	29.4	22.8
26.9	35.9	25.8
32.6	43.8	39.1
-	-	-
70.2	103.1	104.2











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